

PHOTOLYSIS OF PETROLEUM

by

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INTRODUCTION

Of all the weathering processes that act upon oil spilled in the environment, photolysis remains one of the least studied. This in part is due to the fact that in the environment, the weathering processes occur simultaneously, and differentiating the effects induced by photolysis from changes caused by the other processes can be difficult. Studying the role of photolysis is further complicated by the complex composition of petroleum which means a multitude of photo-induced reactions could conceivably take place, producing an array of photochemical products. Recent studies have shown the importance of photooxidation to the overall degradation and ultimate disappearance of oil films from the marine environment (Literathy et al. 1989; Watkinson and Griffiths, 1987).

The general purpose of this study was to examine the chemical and physical changes that occur in oils as a result of photooxidation. A variety of crude oils and petroleum products were used to determine how different oils are affected by photolysis, and to examine the importance of photolysis as a weathering process. Photooxidation products from several oils were isolated and identified.

LITERATURE REVIEW

Petroleum photochemistry

Payne and Phillips (1985) present a comprehensive review of the literature on petroleum photochemistry published prior to 1984. Their review focuses on results from laboratory studies on the photolysis of selected hydrocarbon compounds and of a few oils. Results obtained from oil spills are also summarized. A similar synopsis of the literature can be found in the NRC report "Oil in the Sea" (NRC 1985).

The review presented here will focus upon recent studies. Various effects on oil properties have been attributed to photo-induced reactions. Table 1 summarizes the effects cited in the literature.

Table 1: Summary of reported effects.

Changes in oil colour
Formation of precipitates
Polymerization of components
Solidification of exposed surface
Enhanced water-in-oil emulsification
Increased solubility in water
Increased toxicity
Changes in spreading
Changes in interfacial properties

The list of products reported as a result of the photochemistry of petroleum is extensive. Table 2 lists the general chemical classes of products reported.

Table 2: List of reported photo-products.

Acids
Alcohols
Aldehydes
Carbon dioxide
Diacids
Epoxides
Esters
Hydroperoxides
Ketones
Lactones
Phenols
Polyphenols
Sulfoxides

Table 3 provides a list of precursor compounds and their corresponding products of photooxidation gathered from the literature (Aksnes and Iversen, 1983; Ehrhardt and Petrick, 1984; Ehrhardt and Douadal, 1984; Fukuda et al. 1988; Larson et al. 1979; Lichtenthaler et al., 1989; Moza and Feicht, 1989; Patel et al. 1979; Rontani et al. 1987; Sydnes et al., 1985).

Table 3: List of precursor compounds and corresponding photooxidation products.

Compound	Photooxidation Products
toluene	benzaldehyde benzyl alcohol benzoic acid cresol o-tolualdehyde 3-methylbenzyl alcohol m-tolualdehyde m-toluic acid 3-methyl acetophenone 4-methylbenzyl alcohol p-tolualdehyde 1-phenylethanol acetophenone 1-phenylethanone benzaldehyde 2-phenyl-2-propanol 2-phenyl-propanal 1-phenyl-1-propene 2,4-dimethylbenzyl alcohol 2,5-dimethylbenzyl alcohol 2,5-dimethylbenzaldehyde 3,5-dimethylbenzaldehyde 1-(4-methylphenyl)ethanol 4-ethylbenzaldehyde 1-(3-methylphenyl)ethanol 3-methylacetophenone 1-(3-ethylphenyl)ethanol 3-ethylacetophenone 4-ethylacetophenone 1-(3,4-dimethylphenyl)ethanol 2,4,6-trimethylbenzyl alcohol 1-phenyl-1-propanone 1-phenyl-1-propanol benzaldehyde 1-phenyl-1-butanone 1-phenyl-1-butanol benzaldehyde 1-phenylethanone 1-phenyl-1-pentanone 1-phenyl-1-pentanol benzaldehyde 1-phenylethanone 1-phenyl-1-nonanone 1-phenyl-1-nonanol benzaldehyde n-octane nonanal 1-phenylethanone 1-phenyl-1,4-nonanedione 1-phenyl-1-tridecanone 1-phenyl-1-tridecanol benzaldehyde 1-undecene n-dodecane n-decanal 1-phenylethanone 1-indanone endoperoxide 2-(2-naphthyl)-2-propanol
o-xylene	
m-xylene	
p-xylene	
ethylbenzene	
cumene	
1,2,4-trimethylbenzene	
1,2,5-trimethylbenzene	
1,3,5-trimethylbenzene	
4-ethyltoluene	
3-ethyltoluene	
m-diethylbenzene	
p-diethylbenzene	
1,2-dimethyl-4-ethylbenzene	
1,2,3,5-tetramethylbenzene	
n-propylbenzene	
n-butylbenzene	
n-pentylbenzene	
n-nonylbenzene	
1-phenyl-n-tridecane	
indane	
9,10-dimethylantracene	

Table 3 (continued)

Compound	Photooxidation Products
n-decane	2-decanone
n-dodecane	2-dodecanone
sulfides	sulfoxides
1,8-dimethyl-naphthalene	1,2-benzo-3,7-epoxy-3,3'-dimethyl-4-oxacyclohept-5-ene
	1,4-epoxy-1-methoxy-8-methyl-1,4-dihydronaphthalene
	1,4-dihydroxy-1-methoxy-8-methyl-1,4-dihydronaphthalene
2,3-dimethyl-naphthalene	2-(3-methylnaphthyl)methanol
	3-methyl-2-naphthaldehyde
	2-(3-methylnaphthyl)carboxylic acid
	2,3-dimethyl-1,4-naphthoquinone
	naphtho(2,3-c)furan
1,4-dimethyl-naphthalene	1,2-diacetylbenzene
	1-(4-methylnaphthyl)-methanol
	4-methyl-1-naphthaldehyde
	1-(4-methylnaphthyl)carboxylic acid
2-isopropylnaphthalene	phthalide
	benzoic acid
	phthalic acid

Recent studies by Literathy et al. (1989) and Watkinson and Griffiths (1987) illustrated the importance of photooxidation to the overall degradation of residual oil films on the ocean. It was concluded that photo-degradation may be as important as biodegradation in some cases. The two processes act upon different components in the oil. This can lead to synergistic reactions which enhance the degradation of oil. Alkanes are biodegraded while aromatics tend to be photo-degraded.

Analyses of water samples from areas subjected to chronic petroleum pollution have shown high concentrations of petroleum photo-oxidation products. In one area of intense sunlight, the concentration of photo-products exceeded the petrogenic hydrocarbons by a factor of 10. (Ehrhardt, 1987; Ehrhardt and Douabul, 1989)

Photo-reactivity of Aromatics

Relative to the other classes of compounds found in oil, the photochemical behaviour of aromatic compounds has been rather well studied. When homologous monoalkylated benzenes underwent sensitized photo-oxidation, the main photo-products were 1-phenylalkanones, the corresponding secondary alcohols, benzaldehyde and, when the side chain contained four or more carbon atoms, the products of what is believed to be a Norrish type II photo-degradation (Ehrhardt and Petrick, 1984). The rate and products of photo-oxidation of toluene, xylenes, and cumene were examined by Moza and Feicht (1989). The photo-degradability of these compounds in a film of hexane on water was 10-20% after 3 hours of irradiation by a mercury vapour lamp. The photo-products were oxygenated aromatics, mainly alcohols and carbonyl compounds, that accumulated in the water phase.

The initial photo-reactivity of petroleum distillates was found to be depend upon the aromatic fraction, specifically the mononuclear alkyl benzenes. Photo-oxidation of these aromatics proceeds via a radical chain mechanism in which branching by unimolecular decomposition of hydroperoxides is likely a major part. Photo-oxidation transforms alkyl benzenes into phenones. Polynuclear aromatic compounds were identified as the photo-sensitizing species responsible for most of the initiation reactions. An aromatic-rich distillate photo-oxidized about ten times faster than a homologue distillate with low aromatics content. (Thominette and Verdu, 1984 & 1989; Edilashvili 1982)

Larson et al. (1979) identified hydroperoxides as the principal oxygenated species formed upon short-term irradiation of number 2 fuel oil. Phenolic compounds and carboxylic acids were also identified as photooxidation products. These photo-products significantly increased the toxicity of the water-soluble fractions. Photo-induced toxicity of oil and polycyclic aromatic hydrocarbons has been confirmed by other researchers (Karydis, 1982; Landrum et al., 1986; Newsted and Giesy, 1987; Sydnes et al., 1985).

Studies on the photo-oxidation of diphenylmethane and tetralin as films on water show that oxidation of these compounds is primarily initiated through an excited hydrocarbon/oxygen collision complex which rearranges to hydroperoxides as the primary products. Ketones and alcohols are secondary products. Whereas,

dimethylantracene was oxidized entirely by the singlet oxygen route, forming endoperoxide as the primary product (Arknes and Iversen, 1983).

Generally, pure naphthalenes have a low tendency to photo-oxidize compared to benzylic aromatics. However, the rate of photolysis of alkylated naphthalenes increases several times when the aqueous media is seawater rather than fresh water (Fukuda et al., 1988). The photooxidation of dimethyl-naphthalenes was studied by Sydnes et al. (1985). In the absence of other oil components, photooxidation was found to be very inefficient. In the presence of crude oil, oxidation of the naphthalene moiety predominated due to the abundant formation of singlet oxygen.

Lichtenthaler et al. (1988) found that direct photolysis was the major transformation pathway for the polycyclic compounds dibenzothiophene and 3,6-dimethylphenanthrene. Singlet oxygen concentrations in oil films were high enough to oxidize reactive compounds such as alkylthianes and thiolanes in a few hours. The limiting step in the photo-oxidation of oil films appeared to be the transport of oxygen into the film. Their results suggest that singlet oxygen is a significant source of peroxy radicals compared to direct photolysis.

In studies by Rontani et al. (1985, 1987), it was demonstrated that there was favourable interaction between bacterial oxidation and photo-oxidation during the degradation of alkyl-substituted benzenes. Photo-oxidation products were used by bacteria to form assimilable intermediates.

Photo-reactivity of Alkanes

Nagata and Kondo (1977) established that within crude oil, the secondary and tertiary alkanes are easily decomposed by irradiation when compared to normal alkanes. It is interesting to note that this trend in degradability is the reverse of biodegradation. Normal alkanes are readily degraded by marine bacteria while branched and cyclic alkanes are assumed to be biologically recalcitrant. It was shown that the higher photochemical reactivity of branched alkanes caused a decrease in the pristane/ $n\text{-C}_{17}$ and pristane/ $n\text{-C}_{18}$ ratios of an oil during sunlight irradiation. Traditionally, these ratios are used as indicators of biodegradation, and are not considered to be affected by other weathering processes.

Rontani and Giral (1990) studied the photosensitized oxidation of alkanes in oil films on water. Their study demonstrated that in the case of branched and cyclic alkanes, oxidation acts on the tertiary carbons of these compounds and leads to the formation of tertiary alcohols and to different cleavages of the molecules. It was concluded that photo-oxidation of n -alkanes leads mainly to straight-chain ketones while isoprenoid alkanes form branched ketones and alcohols. A mechanism is proposed that involves an abstraction of hydrogen atom by an excited sensitizer molecule. Aromatic components in oil which have undergone direct photo-oxidation are believed to act as the sensitizers. Tjessem et al. (1983) found that the resin/asphaltene fraction of oil had an appreciable sensitizing effect on the photo-reactivity of n -alkanes. In contrast to this, Lichtenthaler et al. (1988) reported no degradation of n -nonadecane during the irradiation of oil films.

Photo-reactivity of Asphaltics

The asphaltic component of oil strongly absorbs solar radiation and will under photooxidation. The oxidation reaction is not merely a surface molecular reaction, but can result in the formation of a skin of photo-oxidized material of up to about 10 microns in thickness. One consequence of asphalt photo-oxidation is hardening which may lead to cracking and loss of adhesion (Martin, 1971; Mill and Tse, 1990).

Tjessem et al. (1983) showed that the asphaltic components have a sensitizing effect on the photochemical transformations occurring in a crude oil film. Metal porphyrin complexes like those found in the asphaltic fraction can be used as photochemical catalysts for hydrocarbon oxidation (Mansour et al., 1987). A study by Tjessem and Aaberg (1983) found that the asphaltic components of crude oil films are readily oxidized and that new types of asphaltic material are formed during irradiation.

Mechanisms of Photooxidation

Figures 1 to 11 present a number of proposed mechanisms for the photooxidation of petroleum components. These mechanisms include a variety pathways including photosensitizers, free-radicals, singlet oxygen, and ground state triplet oxygen.

**FIGURE 1: Mechanisms of Photooxidation of Petroleum
Including Singlet Oxygen and Radical Processes
Proposed by Larson and Hunt (1978)**

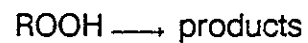
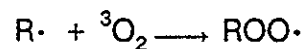
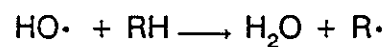
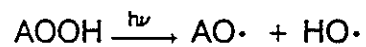
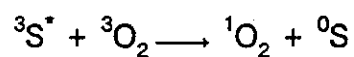


FIGURE 2: Mechanism for Photooxidation of Fuel Oil
Proposed by Larson et al. (1979)

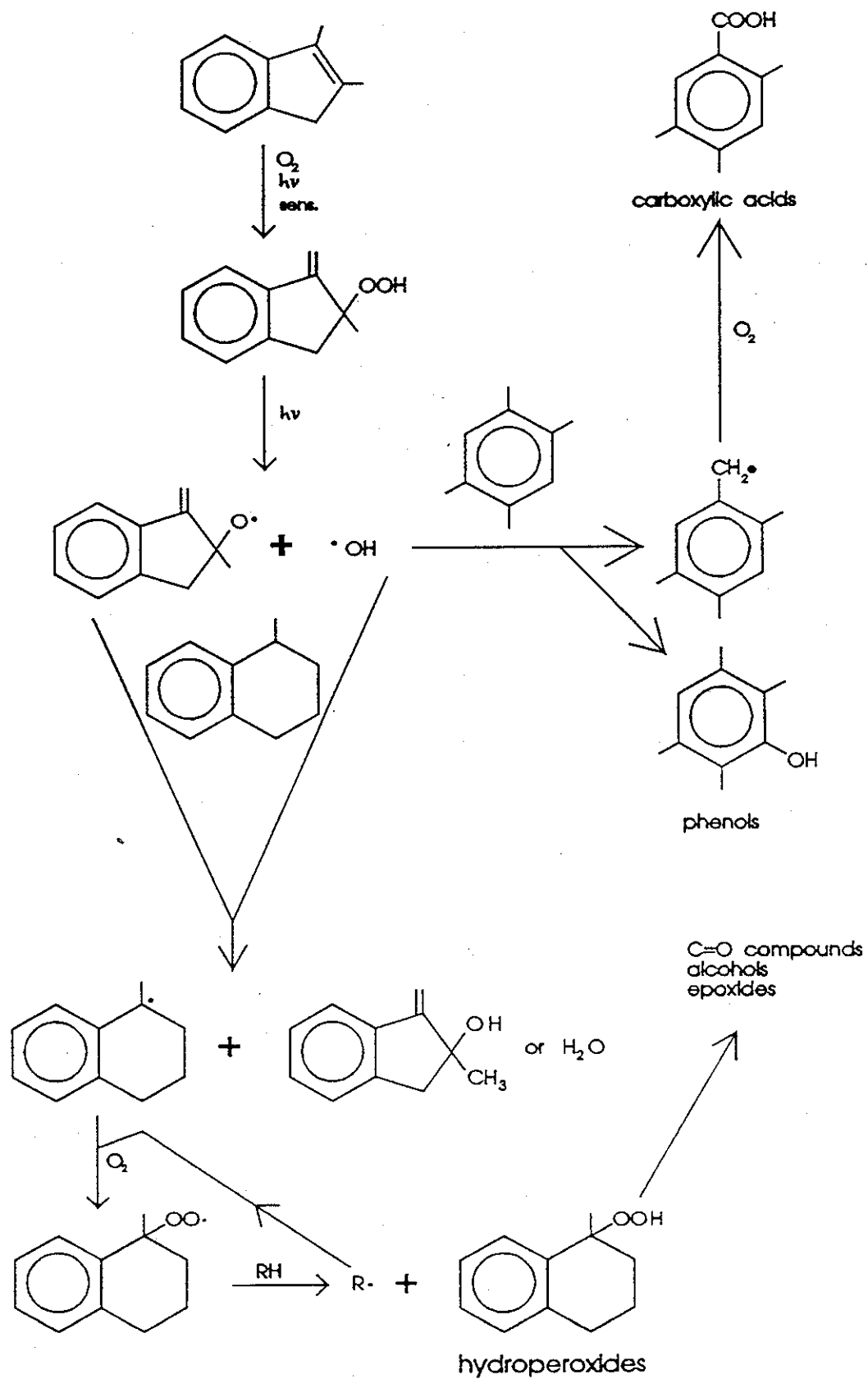


FIGURE 3: Mechanisms for Photooxidation of Petroleum Proposed by Burwood and Speers (1974)

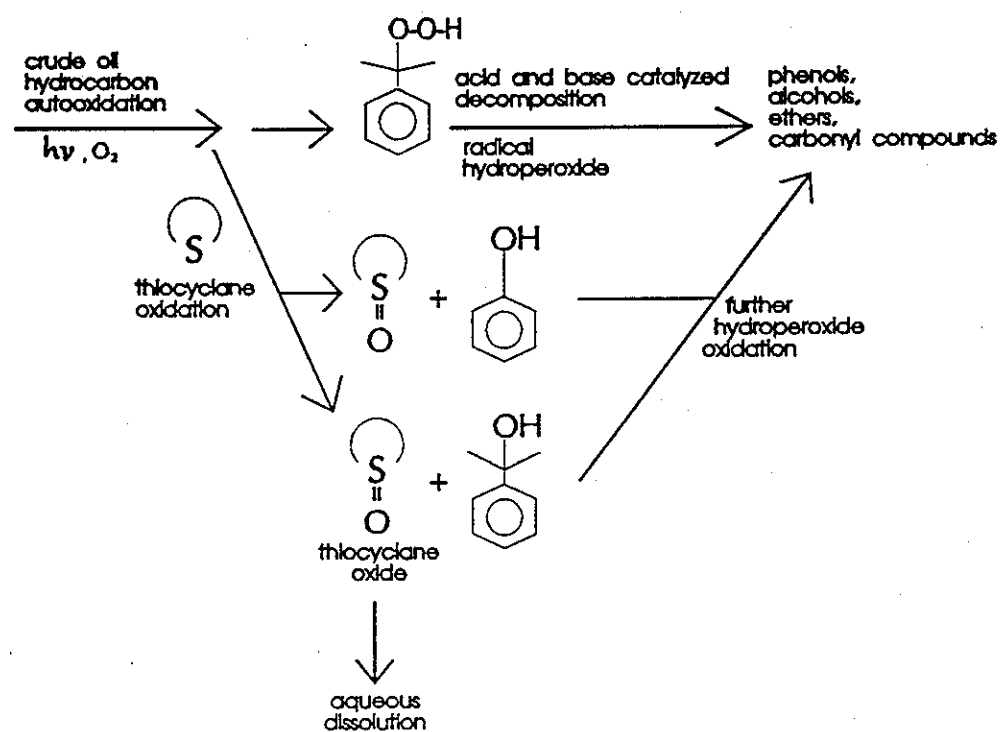
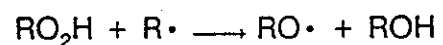
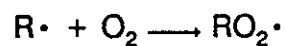
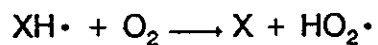
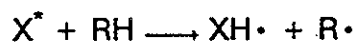
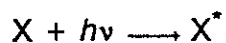


FIGURE 4:

**Photosensitized Oxidation of Hexadecane
Given by Gesser et al. (1977)**



X = xanthone; X^* = xanthone triplet; RH = n-hexadecane.

FIGURE 5:

Mechanism of Photoactivation Involving a
Hydrocarbon - Oxygen Collision Complex which
Rearranges to Hydroperoxide. (Aksnes and Iversen, 1983)

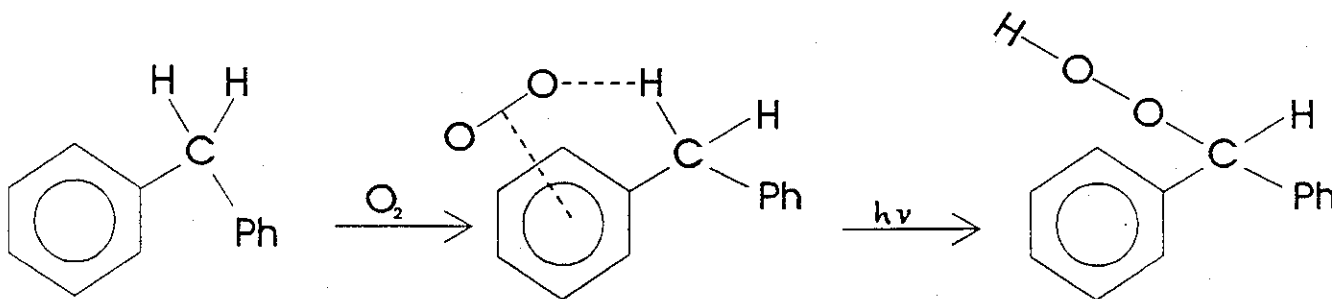


FIGURE 6:

**Mechanism Involving Aleoxy Radical
Proposed by Aksnes and Iversen (1983)**

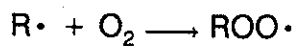


FIGURE 7:

**Mechanism Involving Photo-induced Ketone Triplet
Proposed by Aksnes and Iversen (1983)**

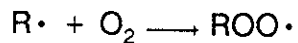
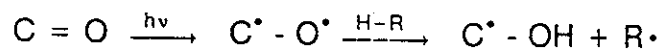
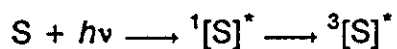


FIGURE 8:

Mechanisms of Photooxidation for Hydrocarbon Mixtures Containing Polynuclear Aromatics
Given by ThomINETTE and Verdu (1984)

Pathway A



where S = molecule absorbing in near-UV.



where PNA = polynuclear aromatic hydrocarbon.



peroxide + $h\nu \longrightarrow$ "stable" oxygen-containing species.

Pathway B

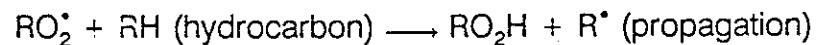
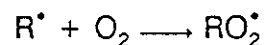
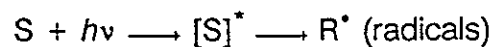


FIGURE 9:

Mechanism of Photooxidation of Dimethyl-Naphthalene Proposed by Sydnés et al. (1985)

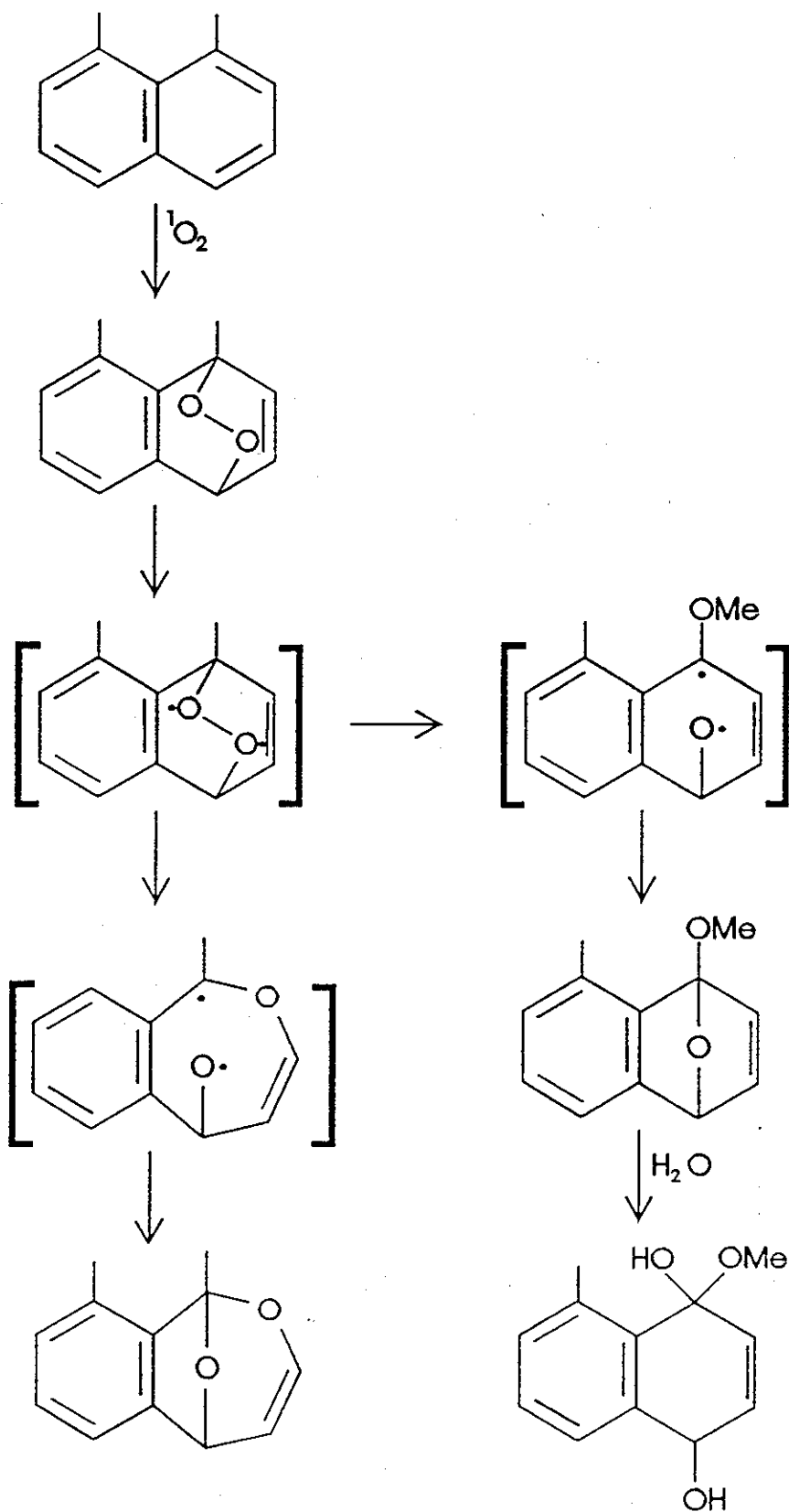


FIGURE 10:

Mechanism of Photooxidation Leading to Formation of Phenones Proposed by Thominet and Verdu (1989)

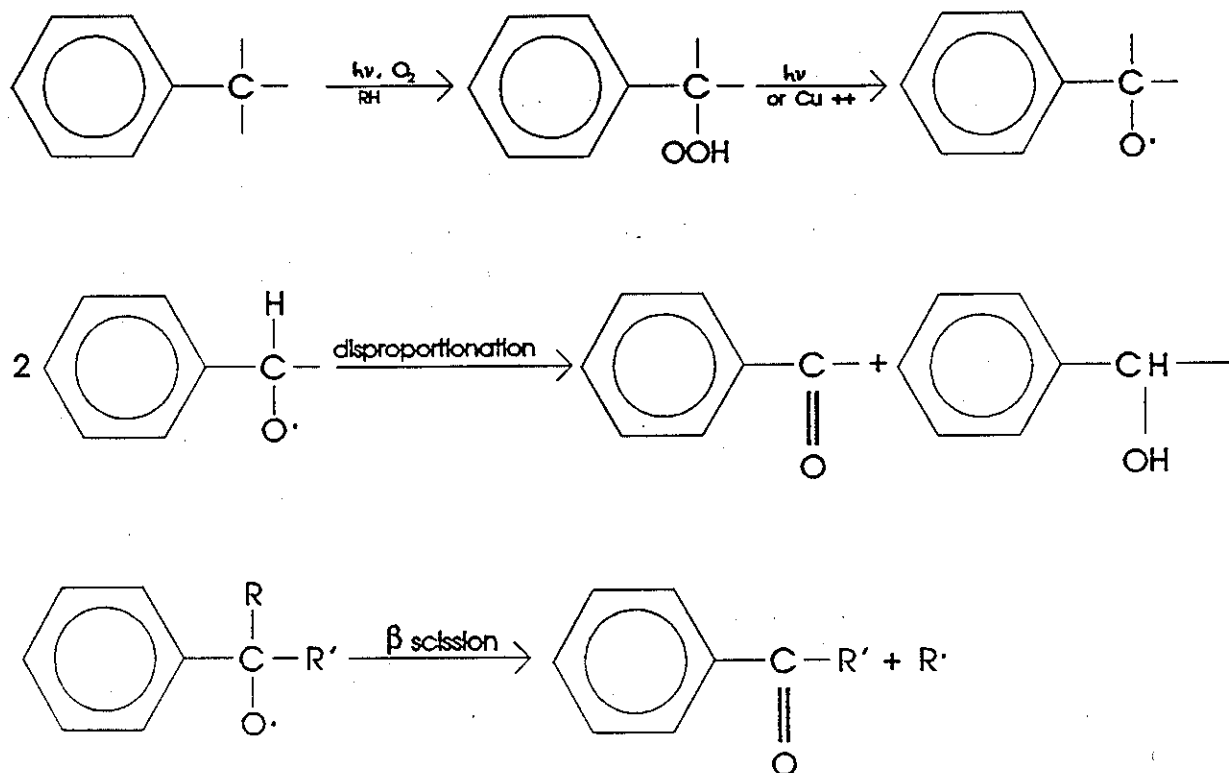
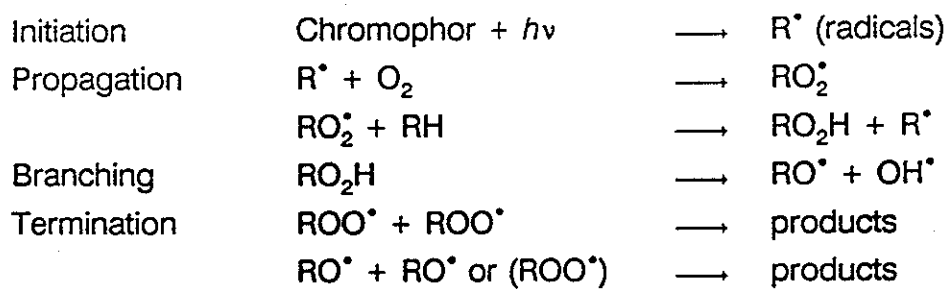


FIGURE 11:

Mechanistic Scheme**Proposed by ThomINETTE and Verdu (1989)**

EXPERIMENTAL SECTION

Materials

The following oils were used in this study:

Adgo Crude Oil (3.0 % by volume evaporated)
Alberta Sweet Mixed Blend Crude Oil (22.8 % by volume evaporated)
Bent Horn Crude Oil (20.6 % by volume evaporated)
Bunker C Fuel Oil
California (API gravity 15) Crude Oil
California (API gravity 11) Crude Oil
Cold Lake Bitumen
Diesel Fuel Oil
Hibernia Crude Oil (16.0 % by volume evaporated)
Prudhoe Bay Crude Oil (14.6 % by volume evaporated)

Oils that are designated as being evaporated were air stripped at room temperature prior to the experiments. The water used in this study was passed through a Millipore purification unit (reverse osmosis, activated carbon and ion-exchange). Bio-crystal marine-mix was added to the water to produce a synthetic sea water of 33 ‰ salinity and 0.02% by weight mercuric chloride was added as an antiseptic. The water was filtered through a 0.2 µm Millipore filter prior to use.

Photolysis

Exposure vessels consisted of 190 mm diameter X 100 mm high, Pyrex crystallizing dishes filled with 2100 mL of water. 26.9 mL of oil was layered upon the water resulting in an initial oil film with an average thickness of 1 mm. The vessel was covered with a 6 mm thick quartz plate which was positioned 8 mm above the rim of the crystallizing dish. The gap between the rim of the dish and the quartz plate was left open to allow normal air flow over the oil surface. A narrow stainless steel tube was inserted into the water layer and held in position so that water could be added to the system without disturbing the oil film if evaporation caused a decrease in the water level. For each oil sample that was exposed to photolysis, a duplicate sample was simultaneously subjected to the same conditions except in a vessel that was completely opaque to light. These samples which were shielded from irradiation were termed "dark controls". The water layer was stirred daily for 90 seconds by a 25 mm egg-shaped stirring bar at 60 RPM. This mixing speed was not of sufficient energy to cause deformation of the oil/water interface for the fresh oils. Some deformation of the interface and shearing of droplets was noticed during mixing of some samples after irradiation.

Photolyses in sunlight were carried out in an unobstructed location free of any reflections or shadows on a roof in Ottawa, Ontario (latitude: 45° 24'N). Experiments were performed during the months of August to mid-October. Sunlight intensity during exposure was measured using p-nitroacetophenone / pyridine actinometry (Dunlin and Mill (1982)).

Experiments were also conducted under fluorescent UVA-340 40-watt lamps (Q-Panel Company) at 22 +/- 2°C. The manufacturer claims that the lamp's emission is an excellent simulation of sunlight from 370 nm down to the solar cut-off of 295 nm.

Selected water and oil samples were examined at various times during the experiment for the presence of microbial activity. No micro-organisms were detected when the samples were subjected to microscopic examination or when inoculated nutrient mediums were incubated.

Analysis

At the termination of each experiment, surface oil was separated from the water phase. The mass of oil remaining on the surface was determined gravimetrically. The water phase was filtered through a 1.0 μm Millipore filter and the mass of "sedimented" oil on the filter was determined. Physical properties were determined for the surface oil samples by the analytical methods listed below:

Property	Method
density	ASTM method D4052-81
viscosity (dynamic)	Brookfield viscometer
interfacial tensions	ASTM method D971-82
asphaltene content	hexane insoluble precipitate

All measurements were determined at 15°C.

The natural dispersibility and chemical dispersibility of selected oils were determined using the Swirling Flask Apparatus described by Fingas (1988) and Enersperse 700 dispersant at an oil-to-dispersant ratio of 25:1.

The oil content of the water phase, after filtering, was monitored using a Horiba OCMA-220 Oil Content Analyzer. The Horiba Analyzer was calibrated using a standard mixture of iso-octane, cetane and benzene. The total carbon content of the water phase was measured using a Xertex-Dohrmann DC-80 Series Carbon Analyzer. The pH of water was also determined.

Aldehydes and ketones in selected aqueous samples were analyzed as their DNPH derivatives (2,4-Dinitrophenylhydrazine) by high performance liquid chromatography (HPLC) by the Pollution Measurement Division of Environment Canada. A Hewlett-Packard 1090L liquid chromatograph coupled to a diode array detector and HPLC Chemstation was used for quantitative carbonyl analysis. The detection wavelength was 360 nm. Carbonyl derivatives were separated with two Dupont zorbax ODS columns (4.6mm X 25 cm) connected in series. A gradient elution program (acetonitrile and water) was used. The program consisted of linear gradient from 60% to 75% in 30 minutes, and then a linear gradient from 75% to 100% acetonitrile in 2 minutes. This was then held at

100% acetonitrile for 5 minutes, reverse gradient to 60% in 1 minute and isocratic at 60% for 15 minutes . The flow rate was 1.0 mL/minute and separations were performed at 30°C. Calibration standards were prepared from purified carbonyl derivatives.

Selected water samples were extracted using multiple batch extractions of ethyl acetate as described by Aaberg et al. (1985), and the extracts were then concentrated under vacuum. These concentrated extracts and surface oil samples were fractionated by gel chromatography using lipophilic Sephadex LH-20 dextran gel and mixtures of chloroform, methanol and ethanol as described Barth et al. (1981). This fractionation technique separates compounds according to degree of polarity.

Samples were analyzed using a Hewlett Packard 5971A Mass Selective Detector with a HP 5890 Series II Gas Chromatograph and a HP 59970 Chemstation. Either a 50m HP-1 or a HP-FFAP (0.2mm inside diameter; 0.33 μ m film thickness) capillary column was used for chromatographic separation. Helium was used as the carrier gas (1 ml/min). The injector temperature was 250°C and the interface temperature was 290°C. A PBM (probability-based matching) search was used with the NBS library containing 49,000 compounds. Calibration was by means of authentic compounds. The mass selective detector was automatically tuned using perfluorotributylamine (PFTBA).

RESULTS AND DISCUSSION

Table 4 summarizes some of the physical manifestations that were attributed to photolysis. Water beneath irradiated oils acquired a yellowish hue. The intensity of this hue varied from oil to oil, and increased with exposure time. Water beneath shielded oils exhibited no colour change. As noted in the table, precipitates formed in some of the oils during irradiation and some oils developed a crust-like formation at the air-oil interface. Neither of these phenomena were observed in the shielded oils.

Table 4: Observations

Oil	Physical Changes During Irradiation
Diesel	<ul style="list-style-type: none"> - within an hour of irradiation the oil's colour began to change from a brownish yellow to a pale yellow and a precipitate formed at the oil/water interface - within six hours the water had a yellowish colour and became turbid - the colour of both the water and oil phases became more intensely yellow with irradiation
Bent Horn Crude	<ul style="list-style-type: none"> - within two hours an orange precipitate was forming in the oil layer - within two days the water had a yellowish colour and became turbid - the oil became more intensely orange and the water more yellow with irradiation
Adgo Crude	<ul style="list-style-type: none"> - within six hours the oil's colour began to change from a medium brown to a brownish orange - within three days the water had a yellowish colour
California 15 Crude	<ul style="list-style-type: none"> - within three days a "skin" had formed at the air/oil interface - within six days the skin becomes slightly encrusted - amount crustal material present increases with time - crustal material flakes off and sinks - after twenty-one days parts of the oil film are overwashed with water and in these areas some bleaching is present - oil beneath crust appears to be relatively fresh - water phase is only slightly coloured
California 11 Crude	<ul style="list-style-type: none"> - same observations as for California 11 Crude but less crustal material is formed
Cold Lake Bitumen	<ul style="list-style-type: none"> - small amount of crust formed - water phase is only slightly coloured
ASMB Crude	<ul style="list-style-type: none"> - small amount of greyish crust formed - water phase is only slightly coloured
Prudhoe Bay Crude	<ul style="list-style-type: none"> - little physical difference between irradiated oil and shielded oil - water phase is only slightly coloured
Hibernia Crude	<ul style="list-style-type: none"> - little physical difference between irradiated oil and shielded oil - water phase is only slightly coloured
Bunker C	<ul style="list-style-type: none"> - small amount of crust formed - water phase is only slightly coloured

Figures 12 to 15 show the change in density as a function of time for exposed oil samples and for shielded oil samples. All samples display an increase in density with time. Increases in density of the shielded (dark) samples can be attributed to the loss of volatile components due largely to evaporation and to a lesser degree, to dissolution. Except for two of the oils, California 15 crude oil and Diesel fuel, the irradiated samples had greater densities than those which were shielded. Possible explanations of why photolyzed oils exhibit greater densities than unphotolyzed oils are probably a combination of effects caused by solar irradiation that include: i. the formation of photooxidation products that are denser than their hydrocarbon parents; ii. the formation of photooxidation products that are easily depleted from the surface oil by evaporation and dissolution; and iii. photolysis enhances evaporation by causing an increase in surface temperature of the oil. The temperatures of oil and water phases were monitored for some oils during the experiment and the maximum recorded difference between exposed and dark samples was 3°C. Possible explanations of why the exposed California 15 crude oil and the exposed Diesel fuel oil were less dense than the unexposed samples are: i. photolysis causes a build up of compounds at the air/oil interface which forms a resistive barrier to evaporation and thereby, reduces volatilization of compounds from the underlying oil; and ii. photo-induced reactions remove dense oil phase compounds. The physical changes noted in several of the oils during irradiation (see Table 4) would provide some support for first theory. Hard crustal material did form on the surface of the California 15 crude oil and the oil beneath this crust was relatively fresh in appearance. No crust formation was observed in the Diesel fuel, but precipitous matter was observed. This precipitous material collected at the oil-water interface and eventually entered the water phase. It could be postulated that this photo-induced precipitation resulted in the removal of the more dense constituents from the oil.

Figure 13: Density versus time

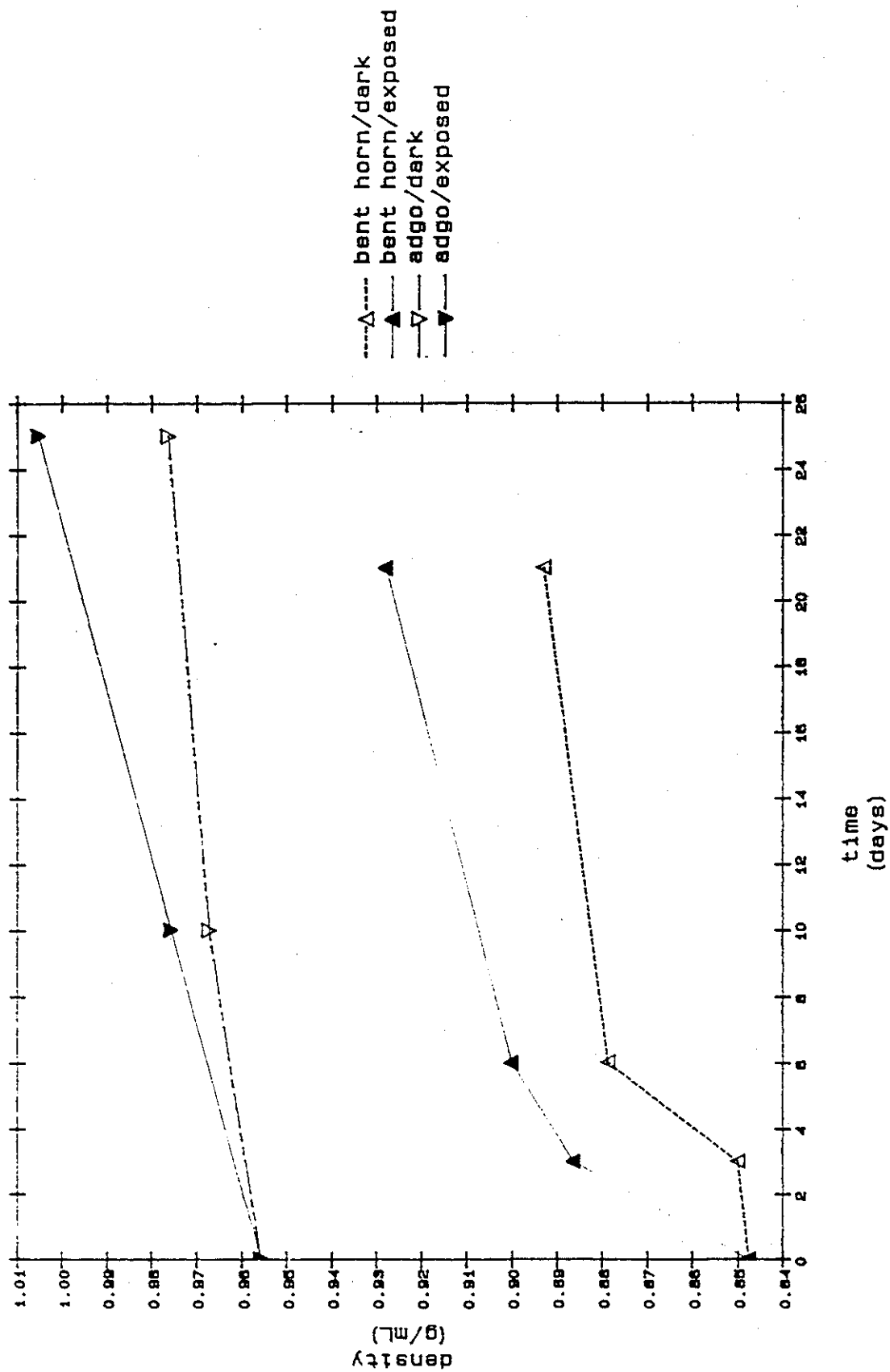


Figure 14: Density versus time

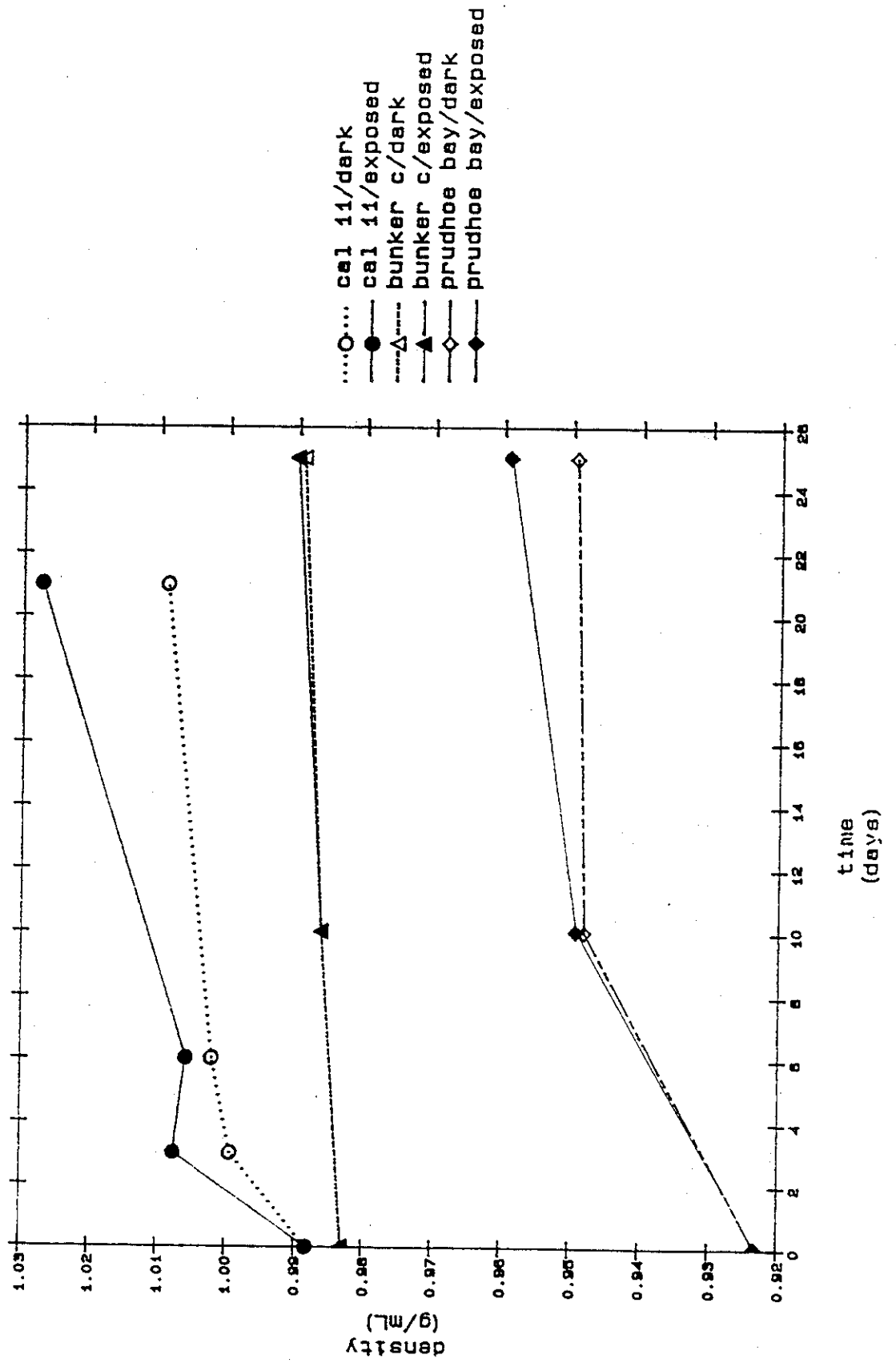
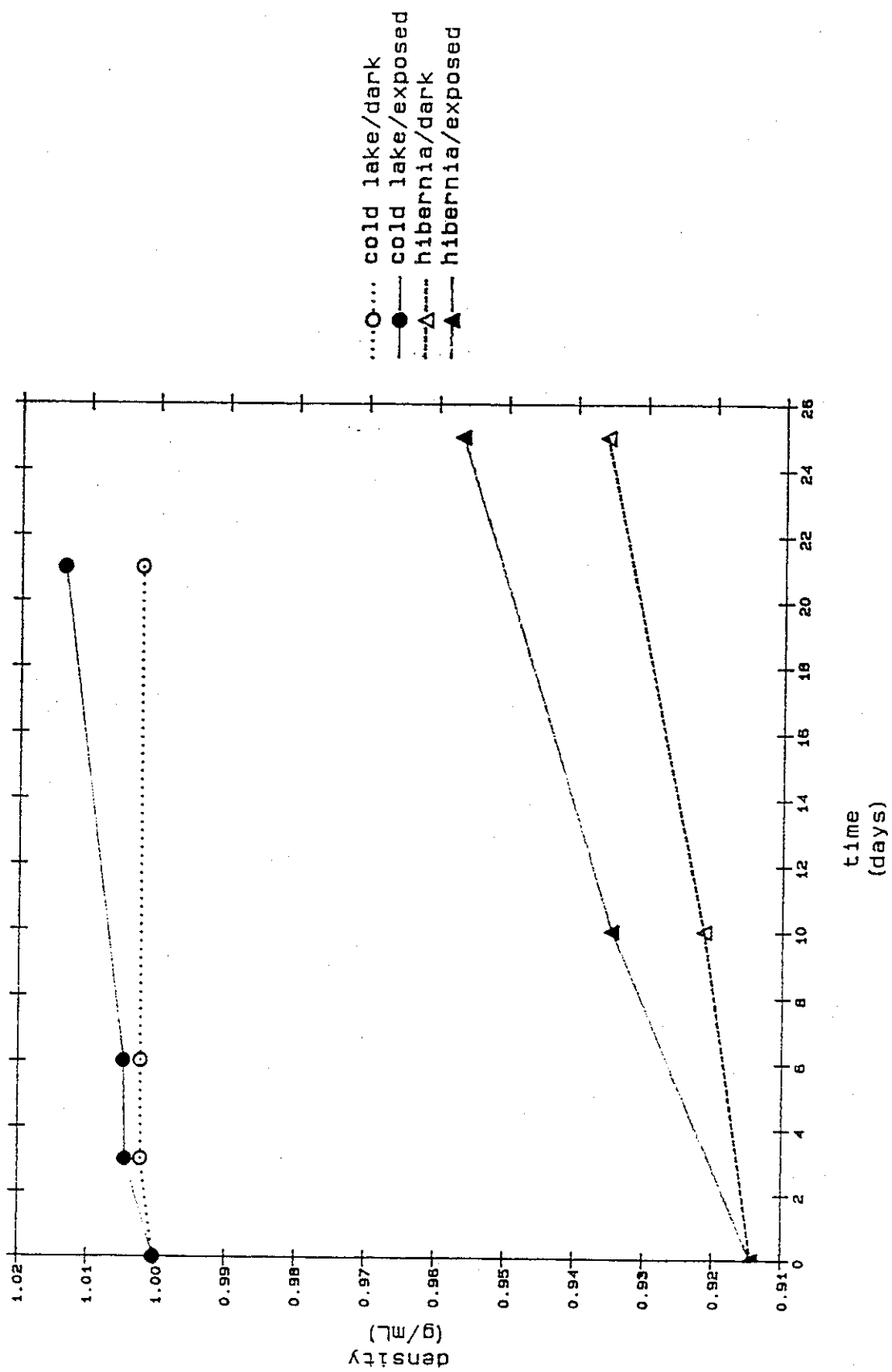


Figure 15: Density versus time



The density measurements also show that several of the oils attained densities that approached or exceeded that of water. California 15, California 11 and Adgo crude oils, and Cold Lake bitumen, all achieved a density of 1 g/mL or greater during the experiments. If these oils were spilled in a marine environment, it is likely that these oils would submerge. As Figures 13, 14 and 15 demonstrate, exposure to solar radiation accelerates an increase in density in some of these oils. The density results obtained in this experiment for California 15 and California 11 crude oils, Bunker C and Cold Lake bitumen are similar to those obtained by Lee et al.(1989).

The measured viscosities of the oil samples are presented in Table 5. For exposure times of 10 days or less, the irradiated oils had significantly higher viscosities than the shielded samples. For exposure times of 20 days or more, the irradiated oils had viscosities that were approximately equal to or slightly less than those of the shielded samples. Photo-polymerization could result in higher viscosity (Daling and Branvik (1988)). The results indicate that effects of photolysis on viscosity over a short term (approximately 10 days or less) can be significant but over a longer term, the effects of photolysis on viscosity will be insignificant compared to the effects of evaporation.

Table 6 presents the measured oil-seawater interfacial tensions. For each oil, the photolyzed sample had a lower interfacial tension relative to the shielded oil. Dramatic reductions in interfacial tensions for the irradiated samples of Diesel, Bent Horn crude oil and Adgo crude oil indicate that photooxidation results in the formation of surface-active products. Daling (1988) demonstrated that these photo-produced surfactants play an important role in the emulsification process.

Table 5:

VISCOSITY (cP)

OIL	CONDITION	TIME (DAYS)					
		0	3	6	10	21	25
DIESEL	DARK	3.00	5.80	9.80	-	-	-
	EXPOSED	3.00	7.60	16.80	-	-	-
BENT HORN CRUDE	DARK	1500	8900	73200	-	108400	-
	EXPOSED	1500	38700	76400	-	78500	-
CALIFORNIA 15 CRUDE	DARK	6400	1400000	>1500000	-	>1500000	-
	EXPOSED	6400	>1500000	>1500000	-	>1500000	-
CALIFORNIA 11 CRUDE	DARK	34000	1100000	>1500000	-	>1500000	-
	EXPOSED	34000	1150000	>1500000	-	>1500000	-
COLD LAKE BITUMEN	DARK	235000	520000	>1500000	-	>1500000	-
	EXPOSED	235000	600000	>1500000	-	>1500000	-
ASMB CRUDE	DARK	135	1800	2750	-	368000	-
	EXPOSED	135	2080	3020	-	387000	-
ADGO CRUDE	DARK	75	-	-	23900	-	-
	EXPOSED	75	-	-	50200	-	-
BUNKER C	DARK	48000	-	-	480000	-	1300000
	EXPOSED	48000	-	-	500000	-	1500000
PRUDHOE BAY CRUDE	DARK	182.5	-	-	1050	-	16500
	EXPOSED	182.5	-	-	2080	-	20000
HIBERNIA CRUDE	DARK	50000	-	-	87000	-	144200
	EXPOSED	50000	-	-	127000	-	113200

OIL - WATER INTERFACIAL TENSION

Table 6:

(mN/m)

OIL	CONDITION	TIME (DAYS)					
		0	3	6	10	21	25
DIESEL	DARK	20.30	24.50	24.70	-	I /S	-
	EXPOSED	20.30	5.10	2.00	-	I /S	-
BENT HORN CRUDE	DARK	13.80	11.80	9.70	-	I /S	-
	EXPOSED	13.80	10.40	2.70	-	I /S	-
ASMB CRUDE	DARK	22.50	26.00	26.50	-	I /S	-
	EXPOSED	22.50	25.40	25.00	-	I /S	-
ADGO CRUDE	DARK	23.10	-	-	16.50	-	22.40
	EXPOSED	23.10	-	-	9.60	-	12.70
PRUDHOE BAY CRUDE	DARK	26.80	-	-	28.20	-	30.90
	EXPOSED	26.80	-	-	25.70	-	27.20
HIBERNIA CRUDE	DARK	16.90	-	-	44.50	-	46.50
	EXPOSED	16.90	-	-	43.70	-	44.70

NOTE: I/ S = INSUFFICIENT SAMPLE

The asphaltene content of surface oil samples are shown in Table 7. Photolyzed samples generally had higher asphaltene contents than shielded samples. This increase in asphaltene content could be due to the formation of macro-molecules by photopolymerization and/or to a concentration effect caused by the removal of photooxidized components from oil. All oils, both exposed and shielded samples, exhibit a general increase in asphaltenes as a function of time, except for Diesel and Bent Horn crude oil. The asphaltene content of Diesel and Bent Horn crude reached a maximum value after 3 days of exposure and then steadily declined with time. This trend is seen in both the exposed and shielded samples.

The natural dispersibilities of the oil samples listed in Table 8 were measured; all of the samples essentially had no natural dispersibility as measured by the Swirling Flask apparatus. Therefore, the photo-produced surfactants present in these oils have no noticeable affect upon natural dispersibility. The chemical dispersibilities of these samples are summarized in Table 8. The effect of photooxidation on chemical dispersibility was extremely dependent upon the oil. The effectiveness of Enersperse 700 on photolyzed Diesel, ASMB crude oil and Prudhoe Bay crude oil was approximately half of the value obtained with non-photolysed samples. Photolysis had no significant influence upon the chemical dispersibility of Adgo and Bent Horn crude oils.

Table 7: **ASPHALTENE CONTENT
(WEIGHT %)**

OIL	CONDITION	TIME (DAYS)					
		0	3	6	10	21	25
DIESEL	DARK	2.43	4.42	2.50	-	1.49	-
	EXPOSED	2.43	4.28	2.07	-	1.38	-
BENT HORN CRUDE	DARK	3.63	4.22	2.64	-	1.56	-
	EXPOSED	3.63	6.27	3.65	-	1.00	-
CALIFORNIA 15 CRUDE	DARK	18.89	24.21	22.60	-	19.50	-
	EXPOSED	18.89	22.87	22.85	-	21.73	-
CALIFORNIA 11 CRUDE	DARK	17.61	19.56	20.86	-	21.98	-
	EXPOSED	17.61	20.67	21.54	-	23.01	-
COLD LAKE BITUMEN	DARK	12.29	13.71	14.81	-	13.59	-
	EXPOSED	12.29	14.94	17.08	-	16.50	-
ASMB CRUDE	DARK	3.55	4.85	4.46	-	4.38	-
	EXPOSED	3.55	6.08	6.15	-	8.21	-
ADGO CRUDE	DARK	2.63	-	-	2.19	-	7.25
	EXPOSED	2.63	-	-	2.25	-	7.28
BUNKER C	DARK	6.33	-	-	6.59	-	6.86
	EXPOSED	6.33	-	-	7.45	-	8.53
PRUDHOE BAY CRUDE	DARK	4.66	-	-	5.72	-	6.02
	EXPOSED	4.66	-	-	6.87	-	9.36
HIBERNIA CRUDE	DARK	3.43	-	-	3.82	-	3.79
	EXPOSED	3.43	-	-	4.51	-	6.25

Table 8: **CHEMICAL DISPERSIBILITY
(WEIGHT % DISPERSED)**

OIL	TIME (DAYS)	DARK SAMPLE	EXPOSED SAMPLE
DIESEL	3	79	43
BENT HORN CRUDE	3	16	19
	6	13	16
ASMB CRUDE	3	19	7
	6	13	7
	21	2	1
ADGO CRUDE	10	22	19
	25	2	2
PRUDHOE BAY CRUDE	10	8	4

Figures 16 to 19 show the amount of oil in water measured by the Horiba Analyzer as a function of time. Similarly, the measured carbon content of water are presented in Figures 20 to 23. Since the water was filtered prior to performing these measurements, only dissolved molecules and sub-micron particles would be present in the water. In each case, the amount of material measured in the water was higher for irradiated samples. As noted in the observations (Table 4), water beneath irradiated oil became yellowish during exposure. The visual intensity of the yellow colour appeared to directly correlate with the measured carbon content. Previous studies have shown that photooxidation products from fuel oils are highly water soluble. (Poston et al. (1988); Herbes and Whitley (1983)) The higher oil content in the water under irradiated oil films suggests that the presence of photooxidized compounds leads to an increase in the amount of oil incorporated into water. The photooxidation products could possibly act as co-solvents which enhance the solubility of hydrocarbons in water. The photooxidation products probably also act as surfactants that stabilize sub-micron oil-in-water emulsions. GC/FID fingerprint tracings indicated that the composition of water extracts were similar to those of the surface oils; this would suggest that some of the oil measured in the water is in the form of oil-in-water emulsions.

Figure 16: Oil-in-water content versus time
Horiba Analyzer results

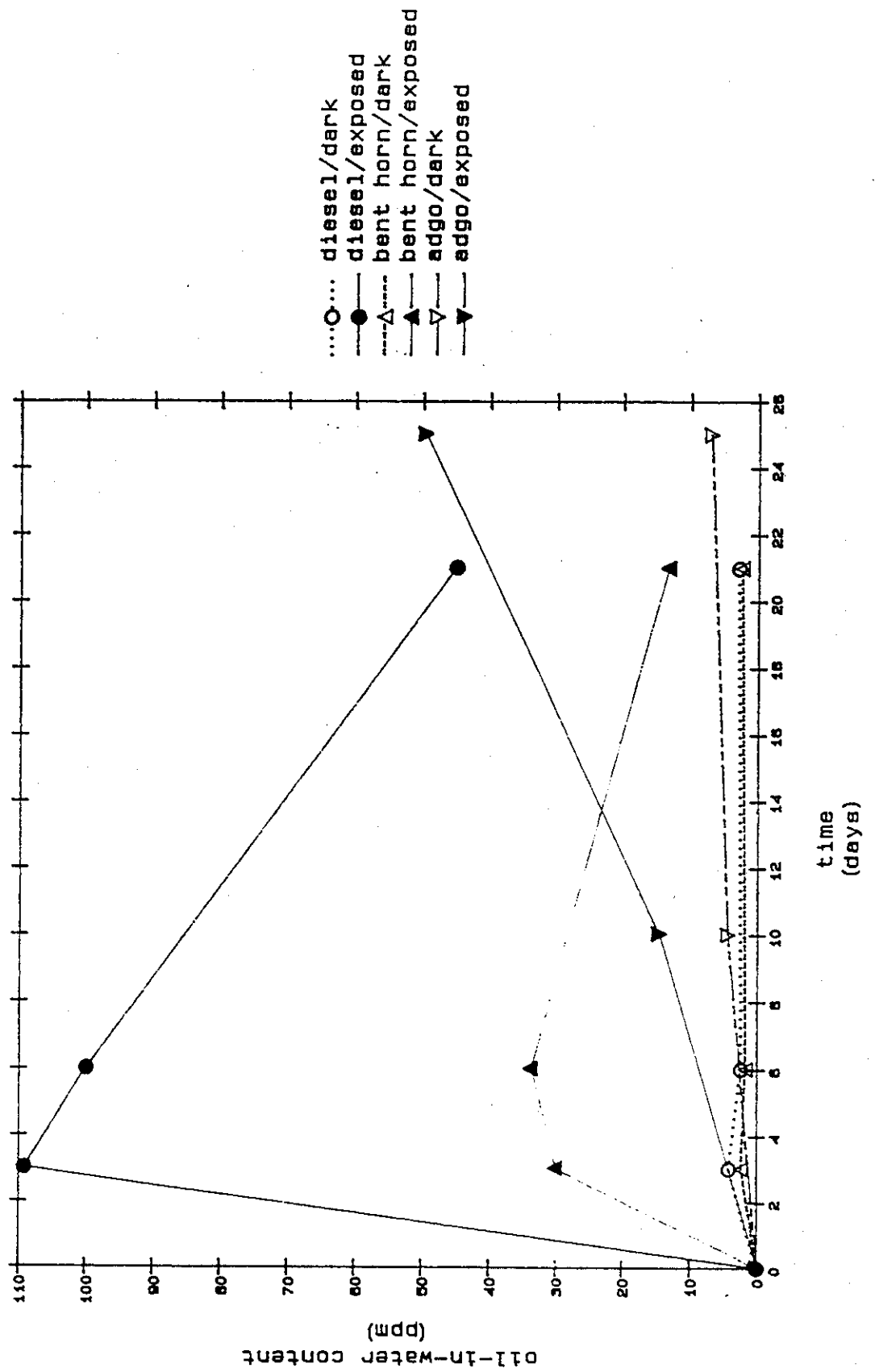


Figure 17: Oil-in-water content versus time
Horiba Analyzer results

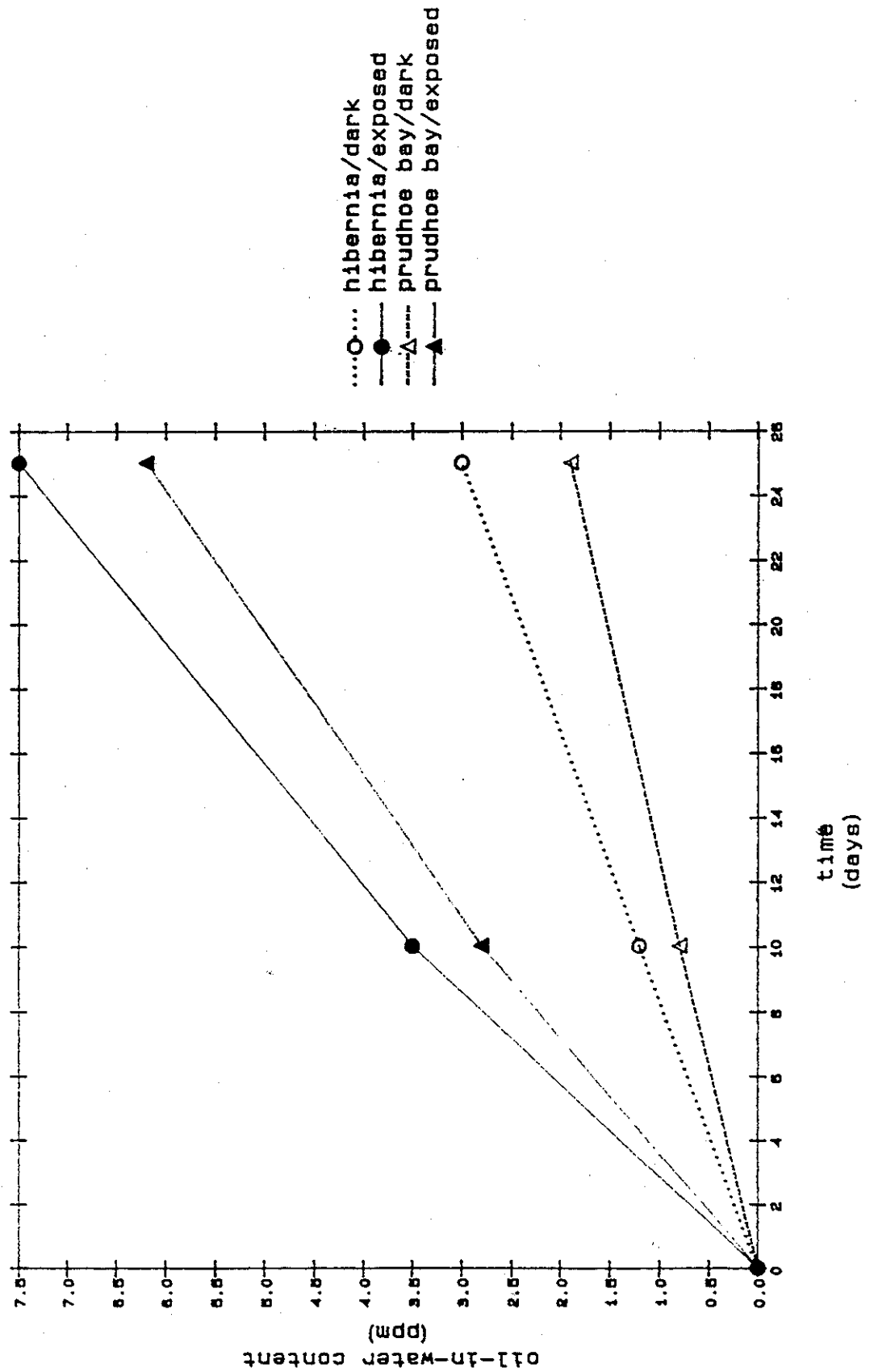


Figure 18: Oil-in-water content versus time
Horiba Analyzer results

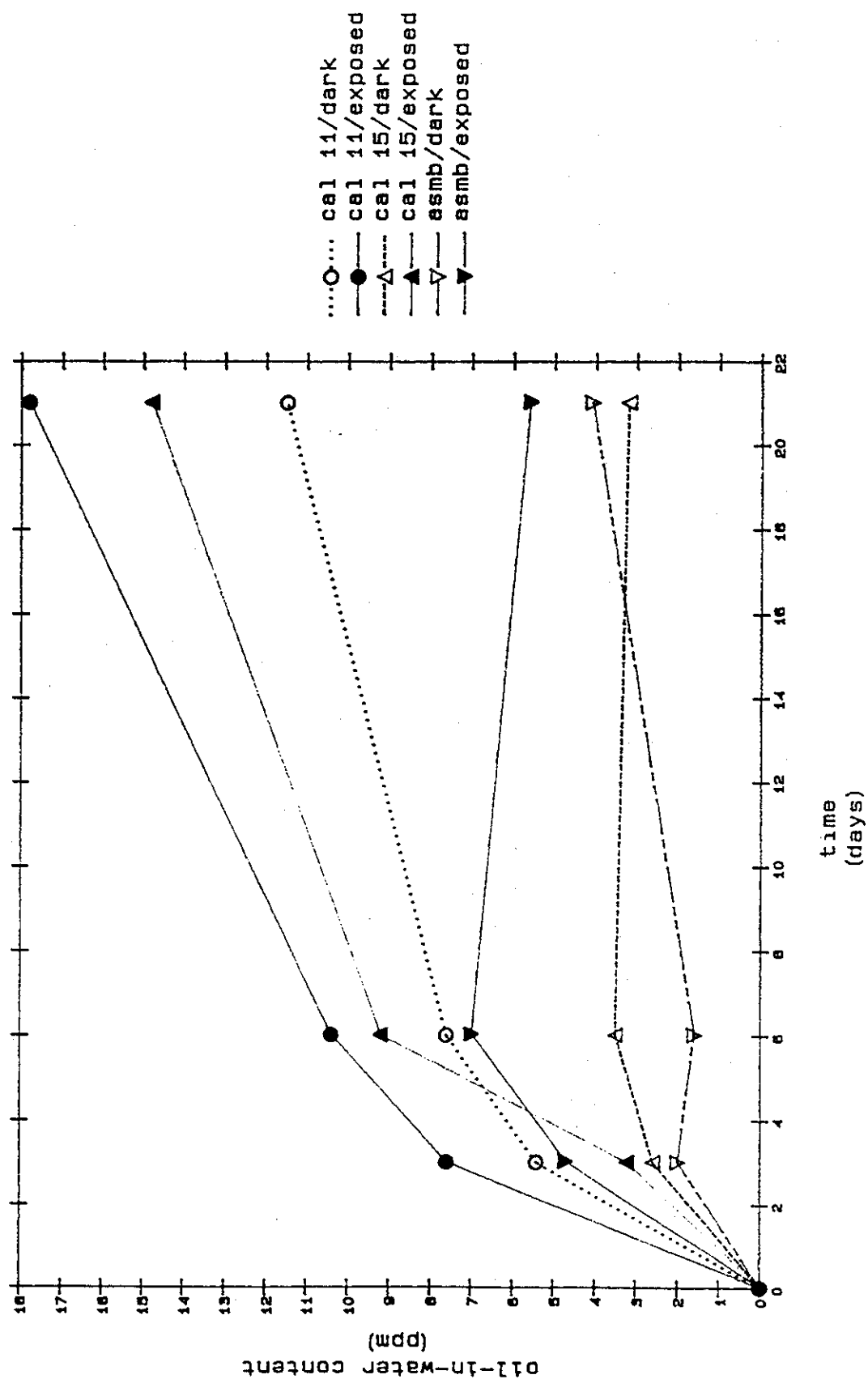


Figure 19: Oil-in-water content versus time
Horiba Analyzer results

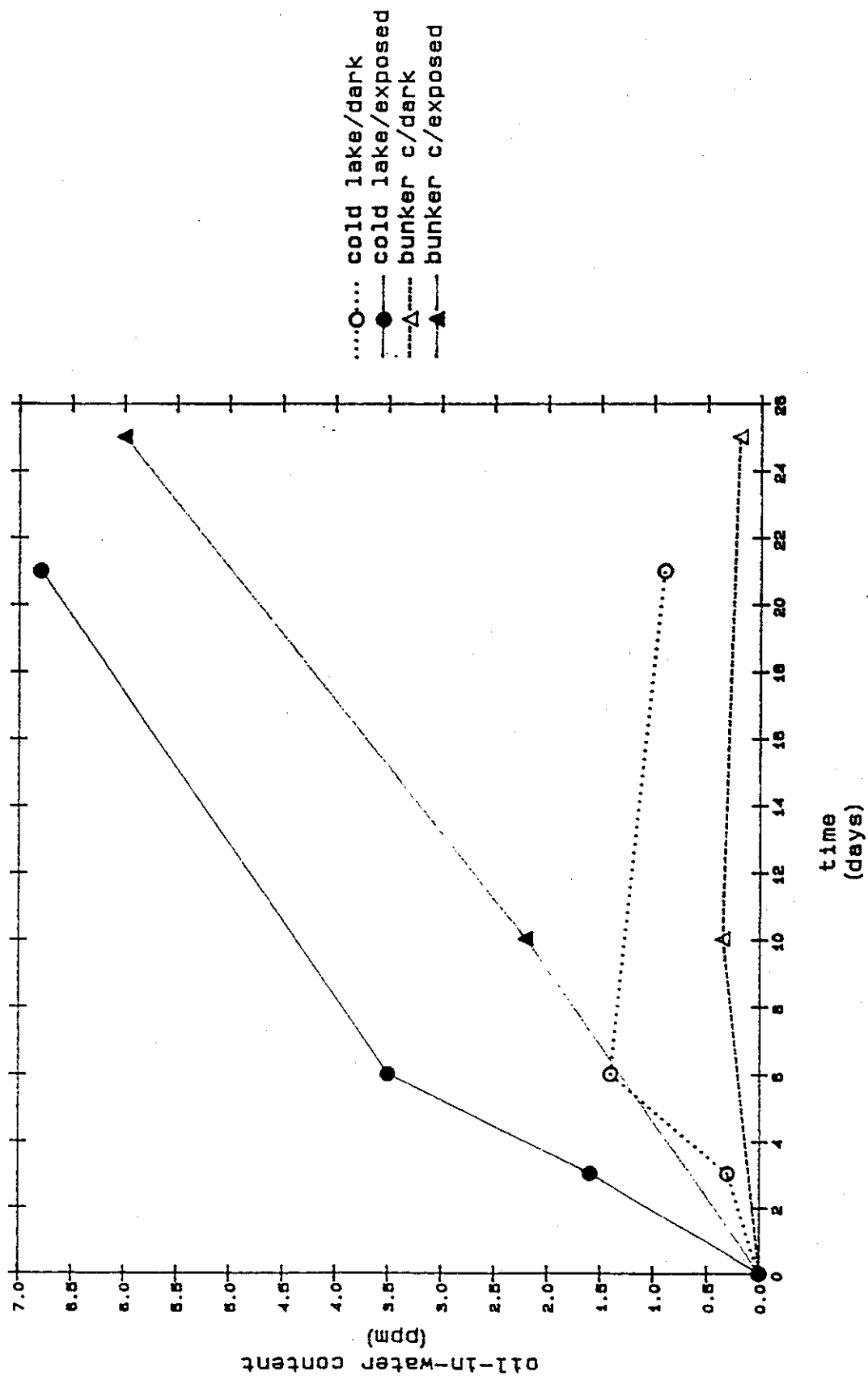


Figure 20: Carbon Content of Aqueous Phase

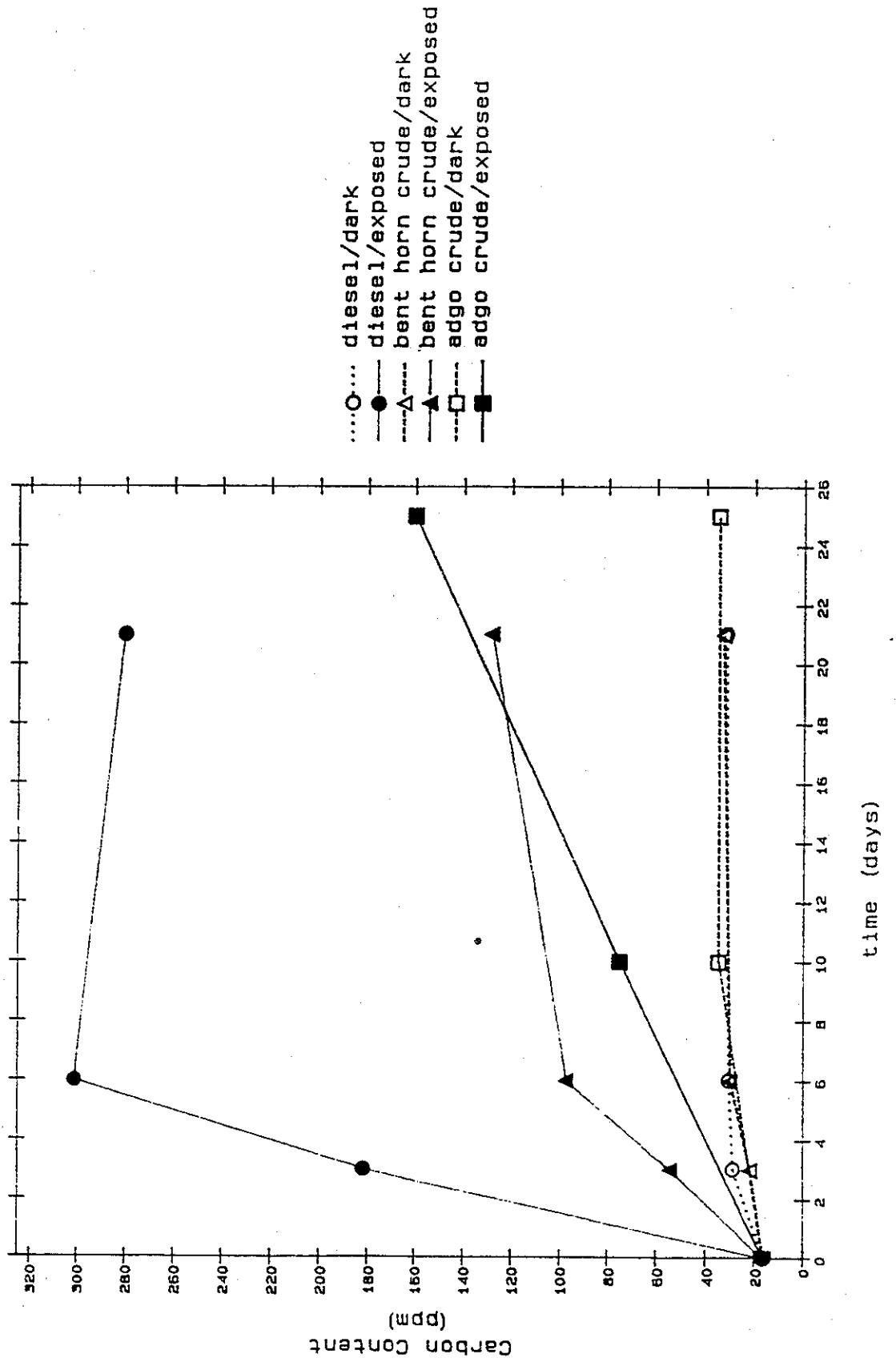


Figure 21: Carbon Content of Aqueous Phase

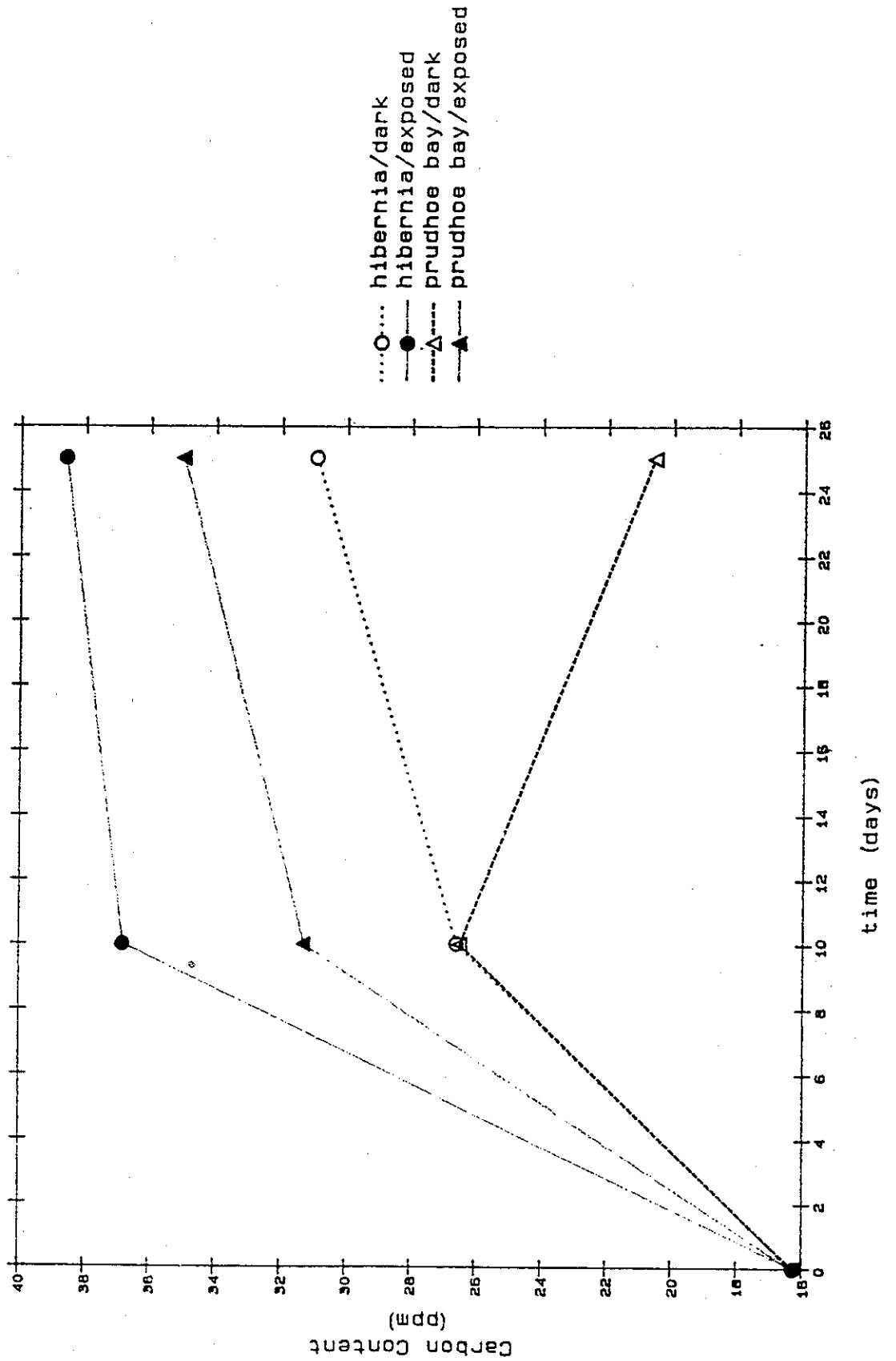


Figure 22: Carbon Content of Aqueous Phase

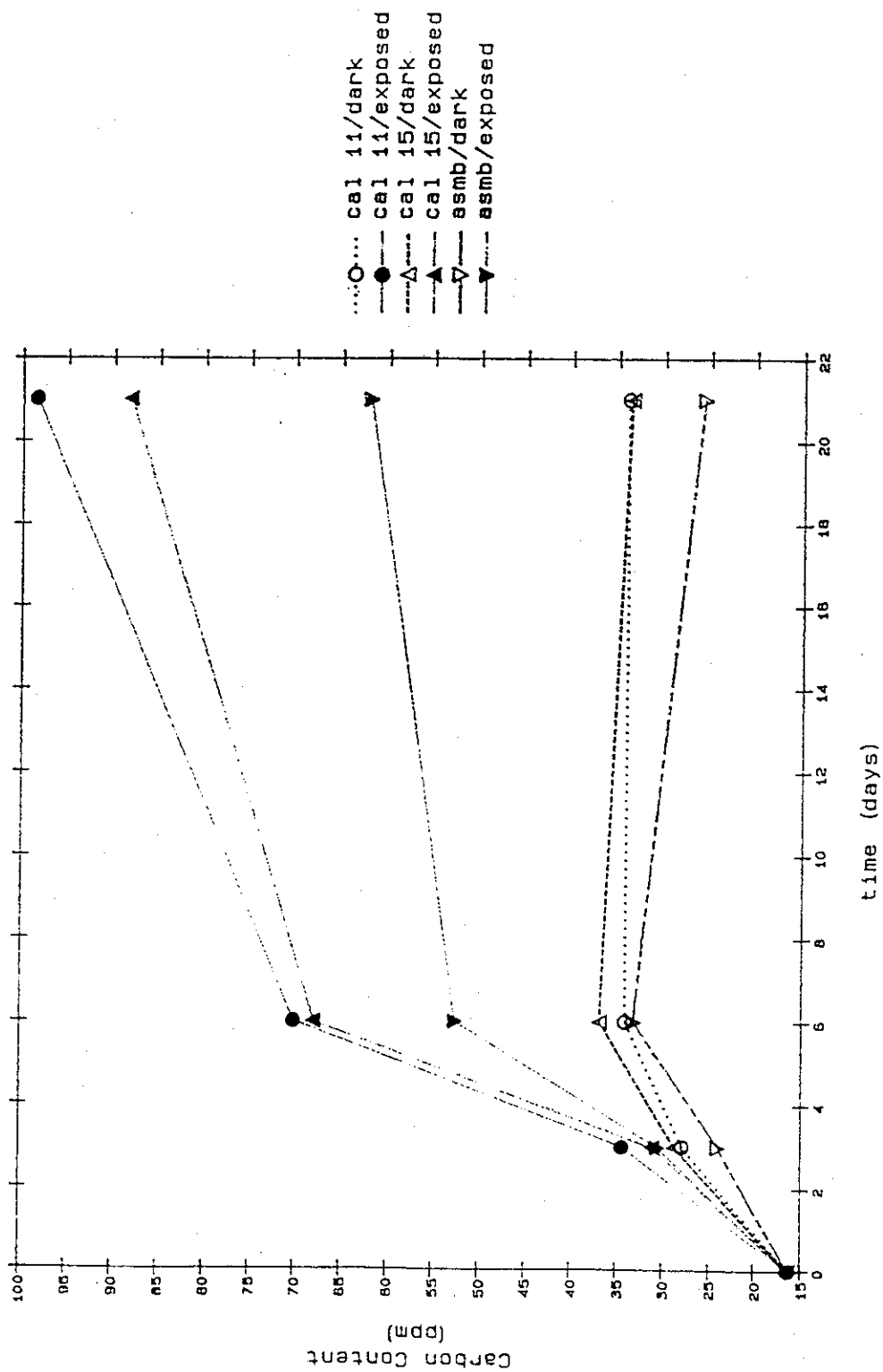
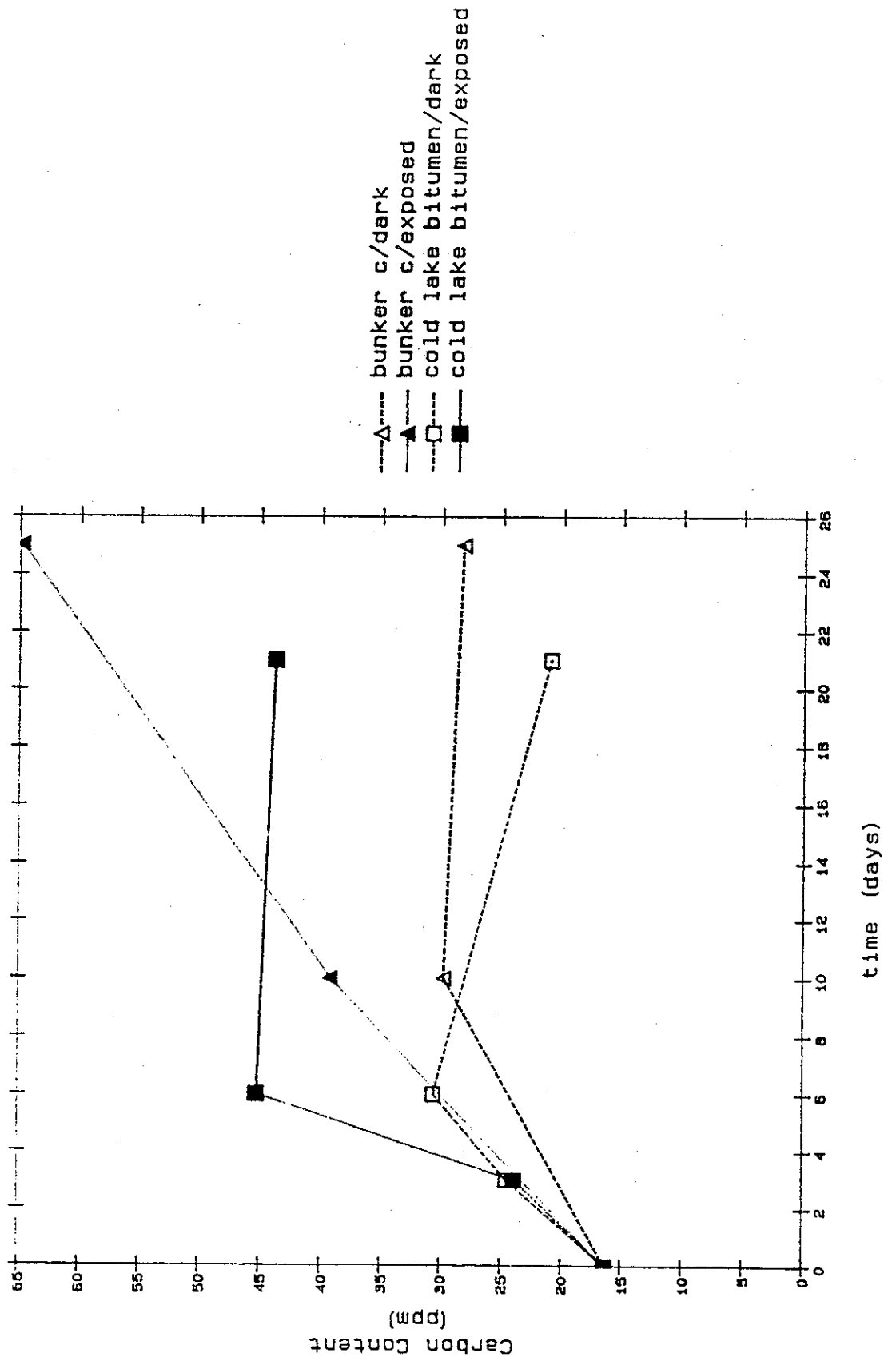


Figure 23: Carbon Content of Aqueous Phase



Changes in the pH of water as a function of exposure time are presented in Figures 24 and 25. The pH of water beneath shielded oils exhibited no change with time and remained constant at a value of 8.5 ± 0.2 . The water beneath Diesel fuel oil and Bent Horn crude oil showed a sharp decrease in pH during irradiation. After 21 days, these water layers had pH readings of about 4. This clearly indicates that the photooxidation products formed by these oils are acidic in nature. The formation of organic acids during fuel oil irradiation had also been noted by Larson et al.(1979). Several studies have compared the toxicity of non-photolysed oil to photolysed oil, and they have shown that photolysis enhances toxicity. Our results indicate that if the species used in bioassays are sensitive to pH, the simple change in pH might be a factor. Under real marine spill conditions, it is unlikely that changes in pH would occur because of the buffer effect from surrounding water.

Figure 24: pH of Aqueous Layer

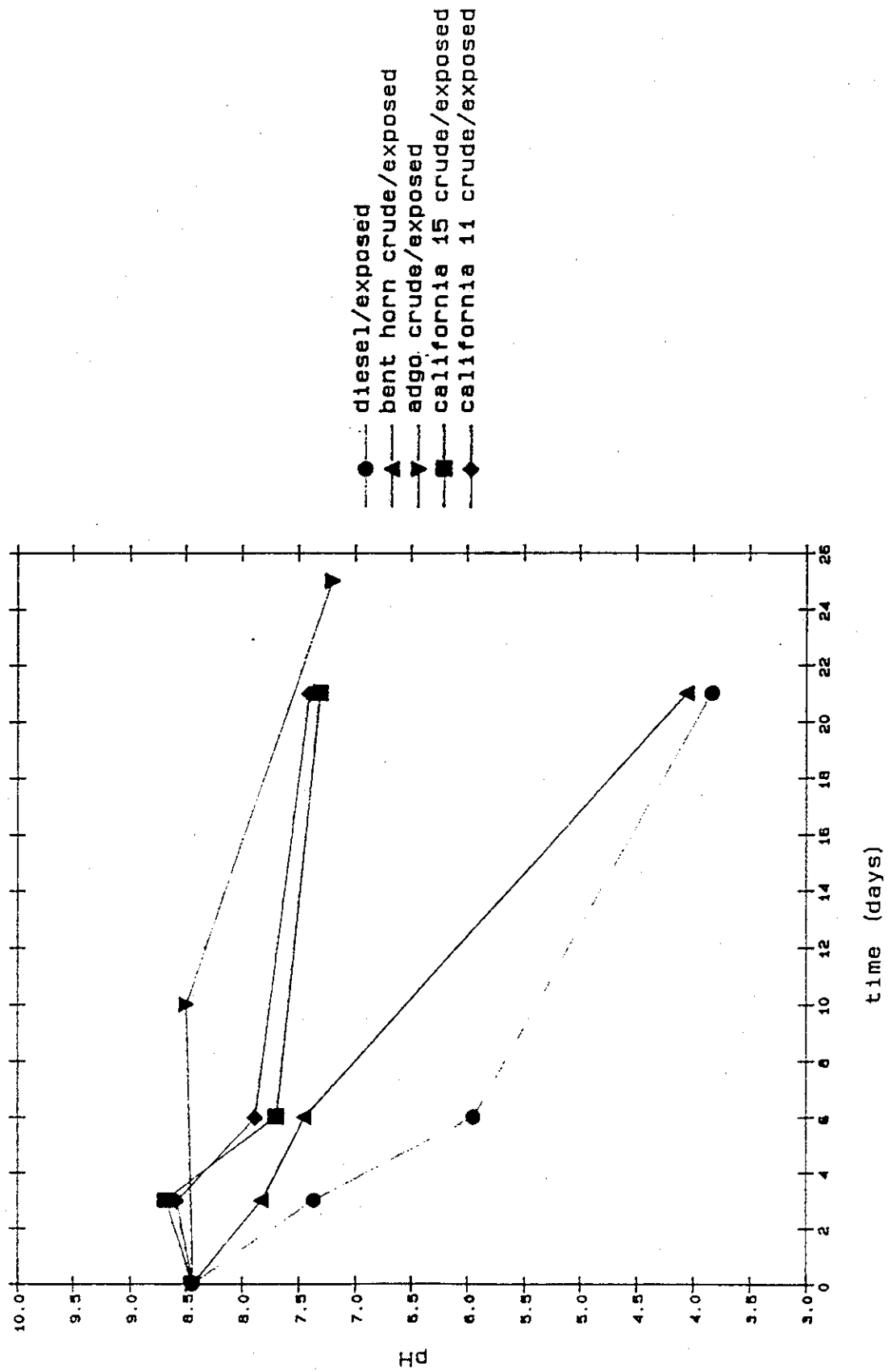
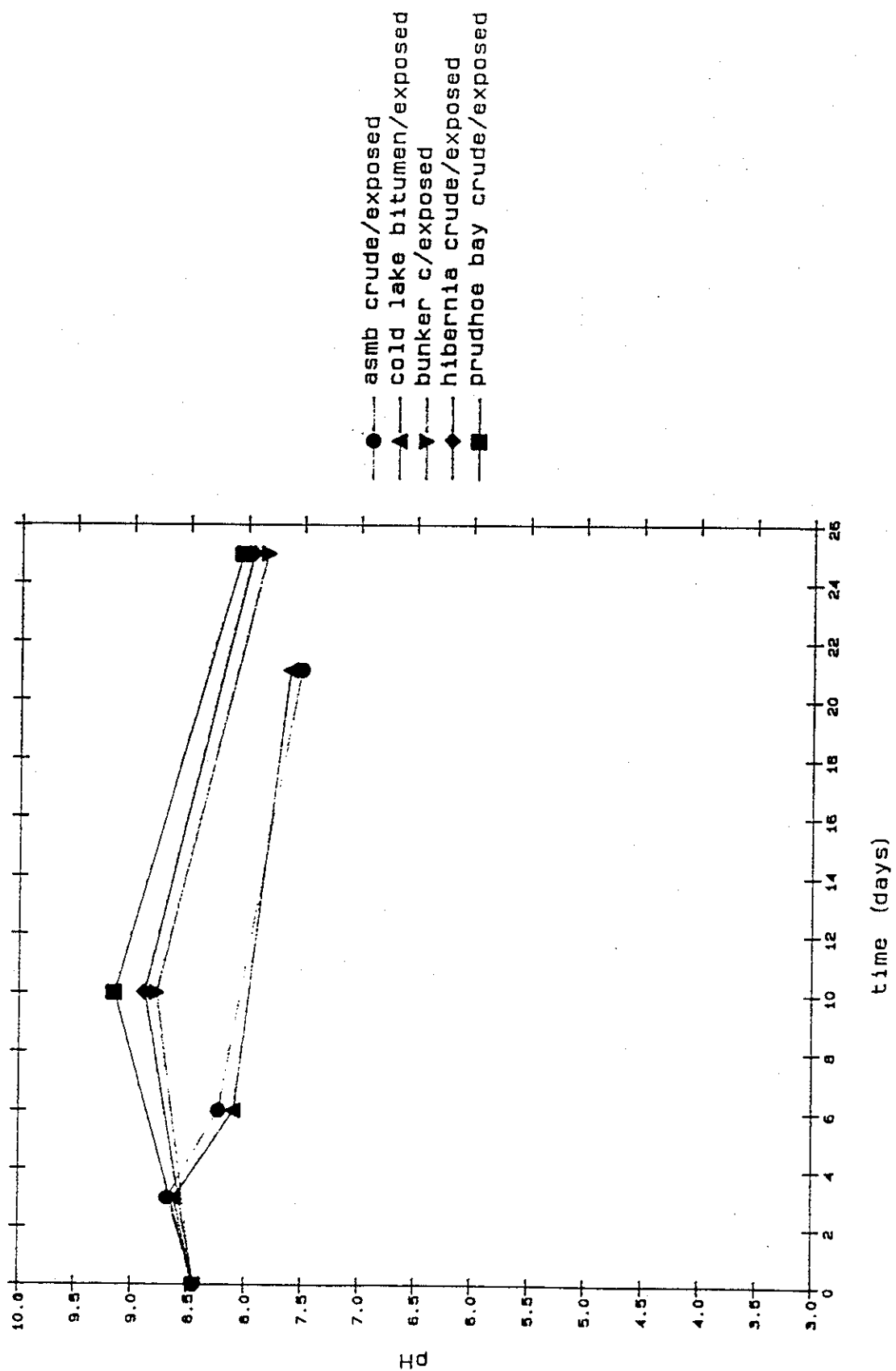
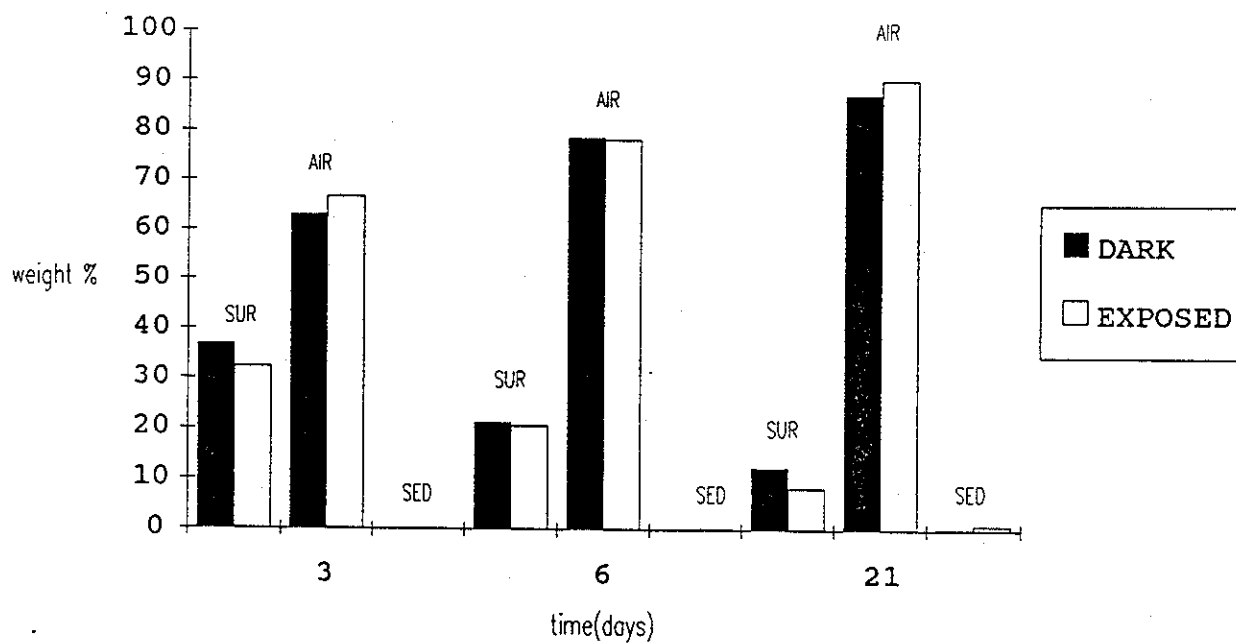


Figure 25: pH of Aqueous Layer



Although the results show that photolysis can significantly influence the amount of oil that enters the water column through dissolution and emulsification, a mass balance shows this quantity to be far less than 1% of the total mass of oil spilled. Figures 26 to 35 show a mass balance for each oil. Each graph illustrates what percent of the original mass of oil remained on the surface as a film (labelled 'SUR' on the graph); what percent of the oil evaporated ('AIR'); and what percent of the oil sank ('SED'). The quantity of oil that evaporated was calculated from the amounts measured in the other phases. At time zero (0 days), 100 % of the oil was on the surface. It should be again be mentioned that some of the oils were artificially evaporated prior to being used. This amount of pre-test evaporation is not included in these calculations. From these graphs, it is apparent that the importance of photolysis to the fate of an oil is dependent upon the oil itself. Exposure to solar radiation resulted in an increase in the amount of oil that "sedimented". Shielded oils had little sediment ($< 0.1\%$). Significant amounts of sedimented oil formed when California 11 and California 15 crude oils were irradiated; after 21 days of exposure, the percentage of oil that sedimented was 7 and 9 %, respectively.

Figure 26: Mass Balance for Diesel Fuel Oil.



AIR = Air
SED = Sediment
SUR = Surface

Figure 27: Mass Balance for Bent Horn Crude Oil.

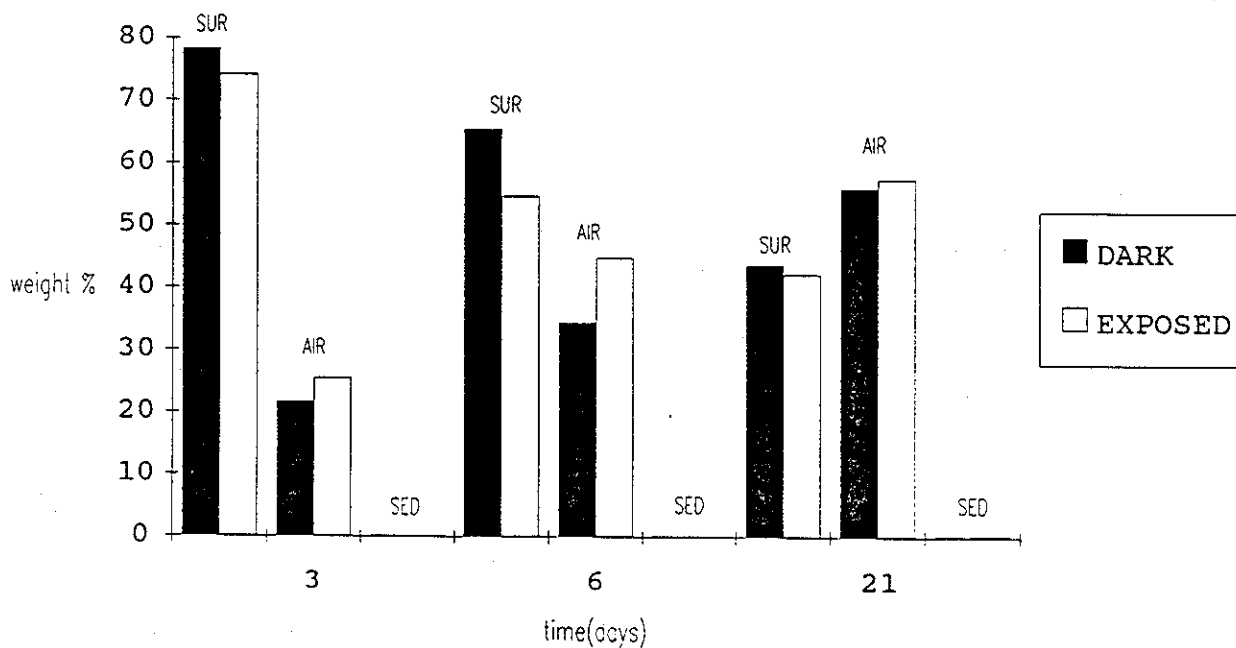
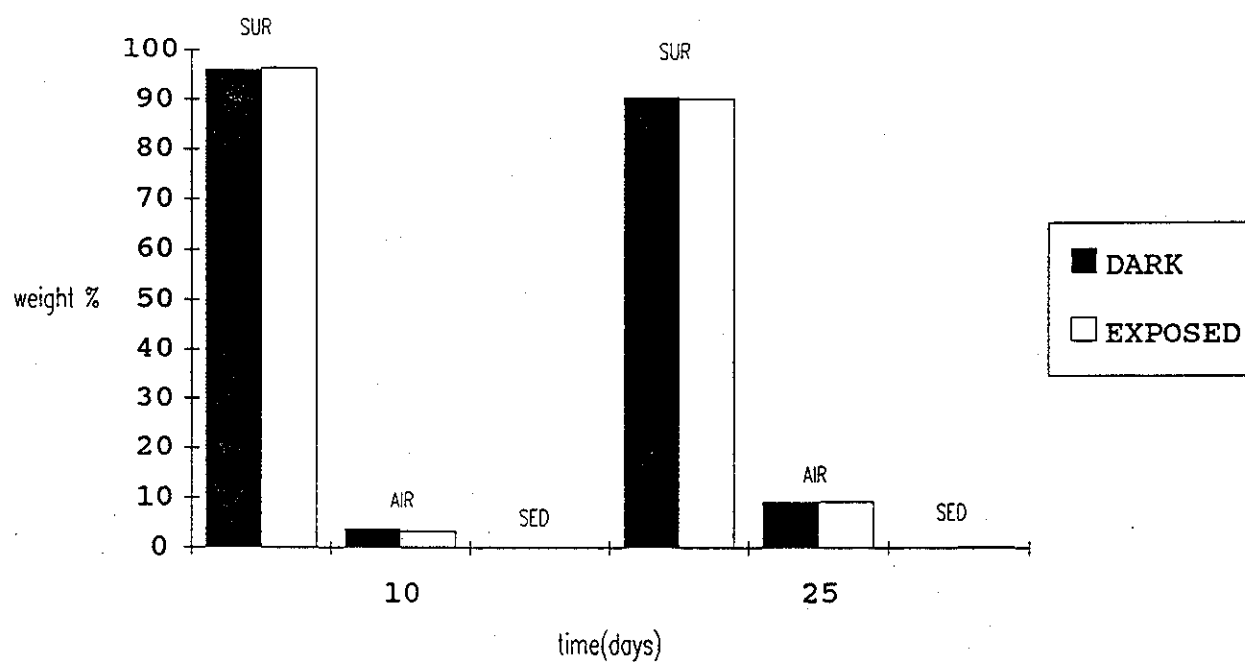


Figure 28: Mass Balance for Adgo Crude Oil.



AIR = Air
SED = Sediment
SUR = Surface

Figure 29: Mass Balance for California 15 Crude Oil.

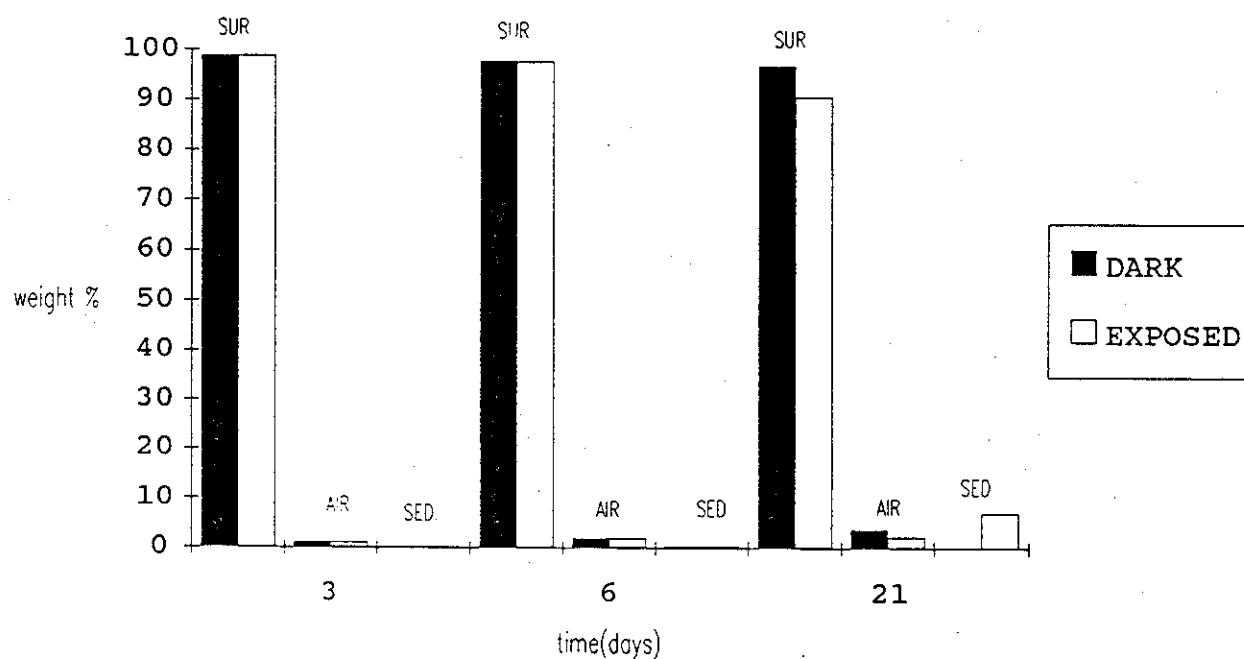
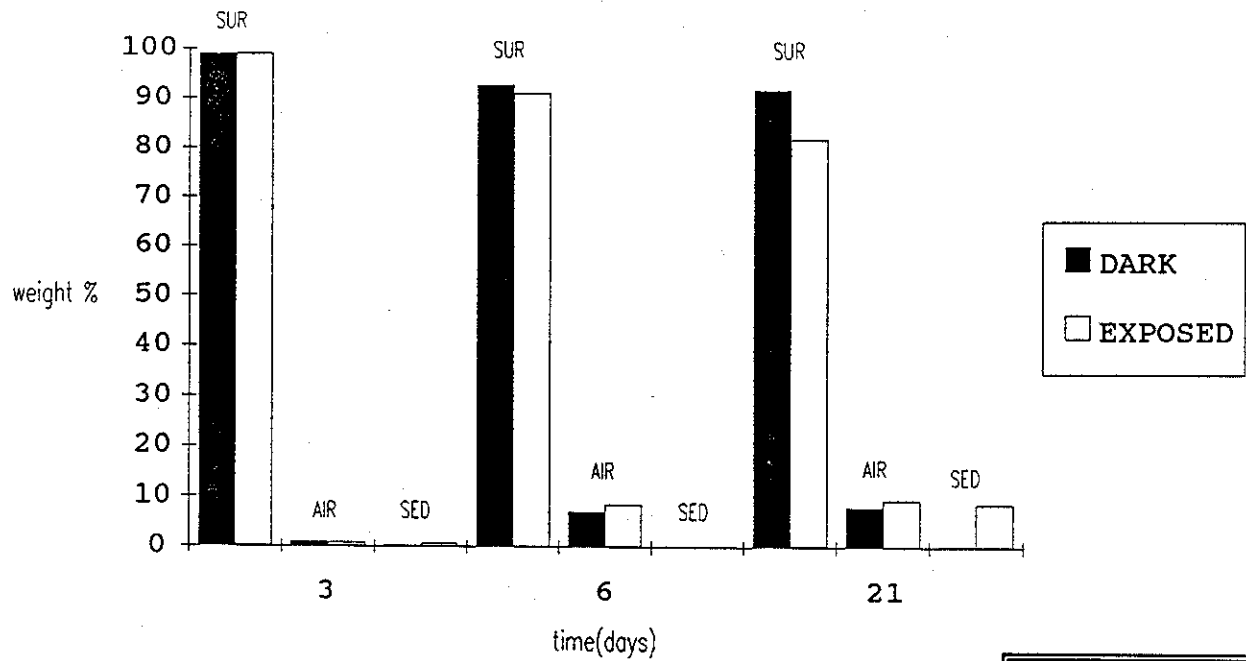


Figure 30: Mass Balance for California 11 Crude Oil.



AIR = Air
SED = Sediment
SUR = Surface

Figure 31: Mass Balance for Cold Lake Bitumen.

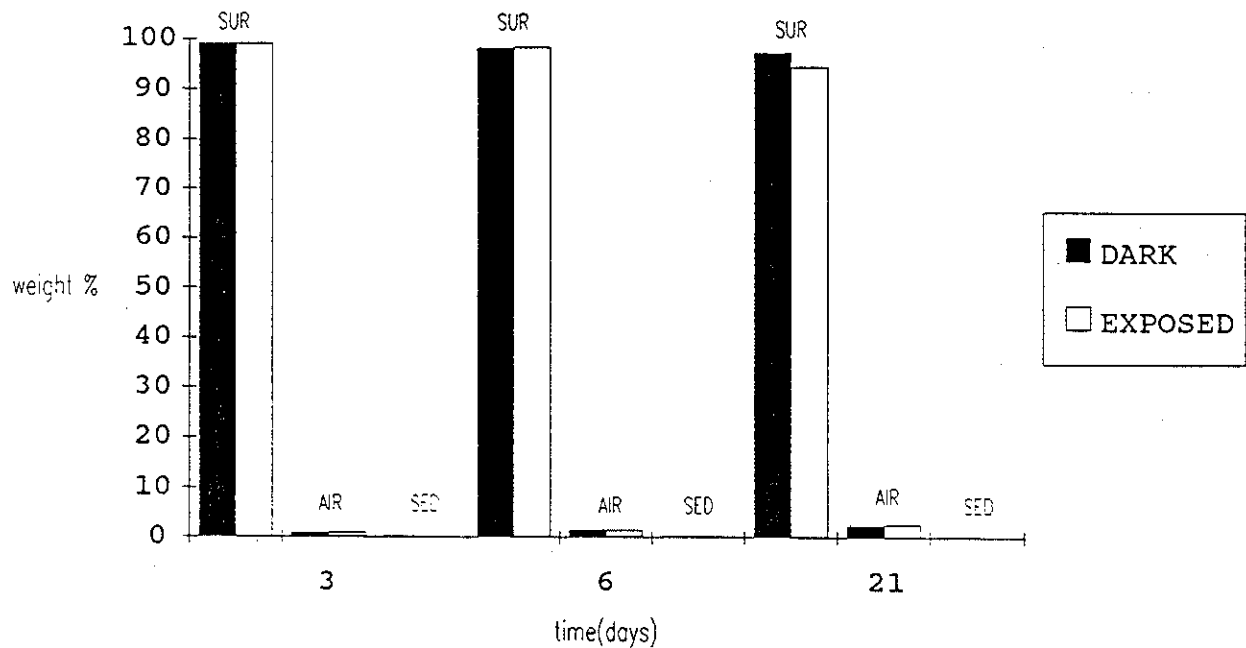
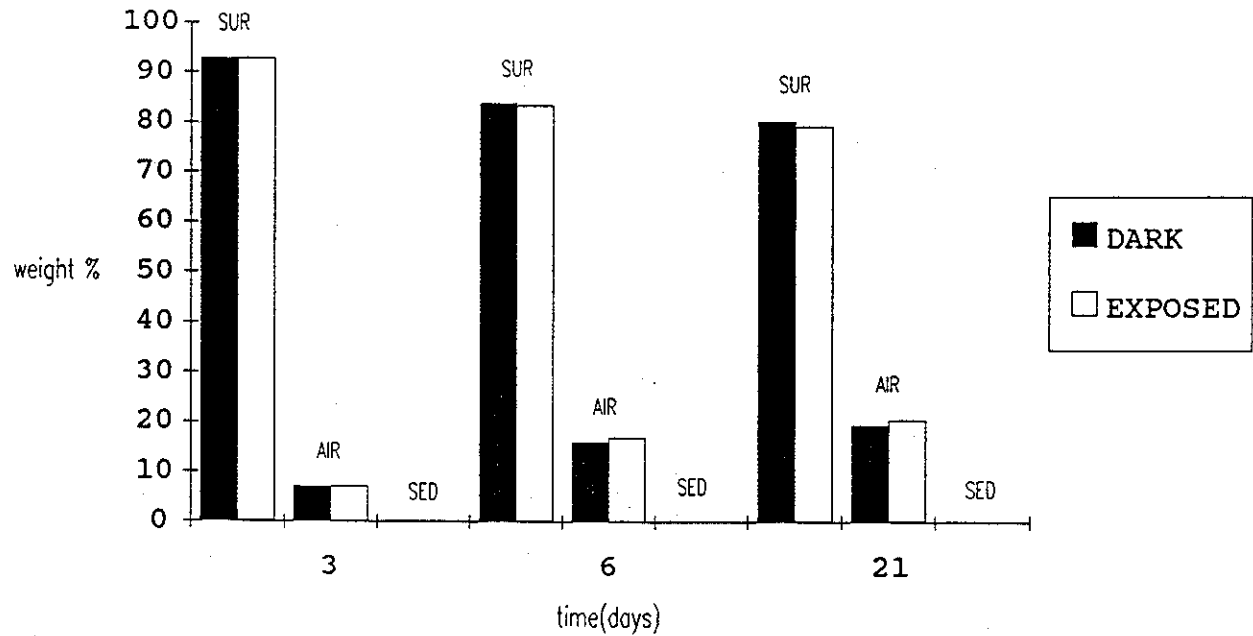


Figure 32: Mass Balance for Hibernia Crude Oil.



AIR = Air
SED = Sediment
SUR = Surface

Figure 33: Mass Balance for Bunker C Fuel Oil.

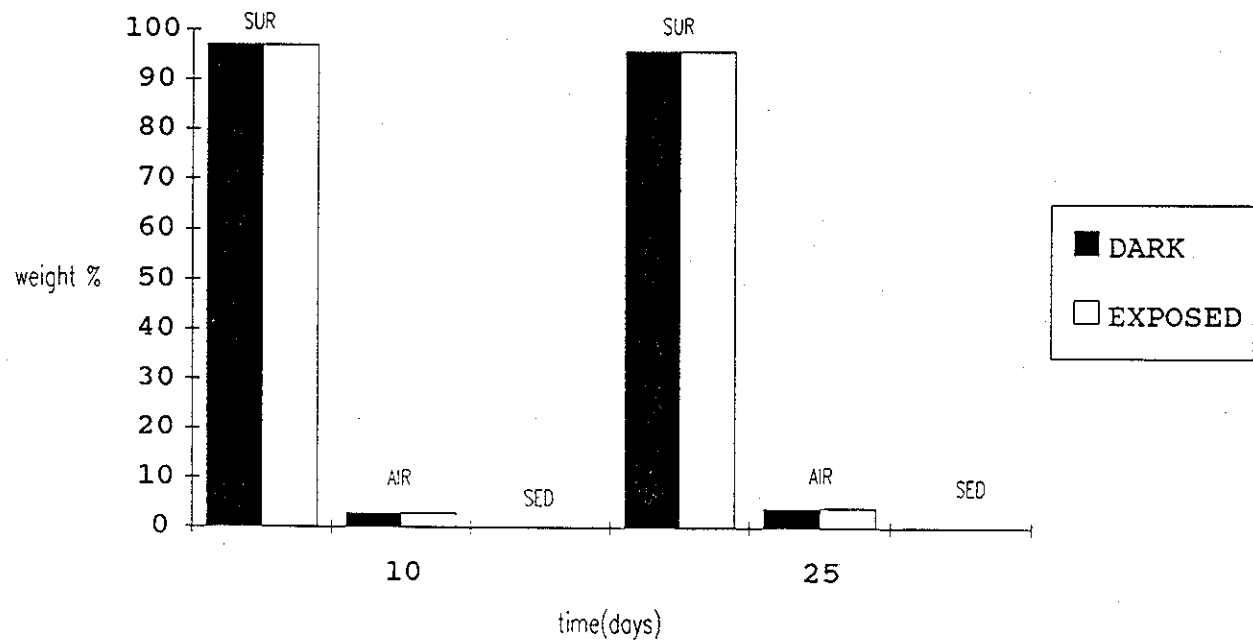
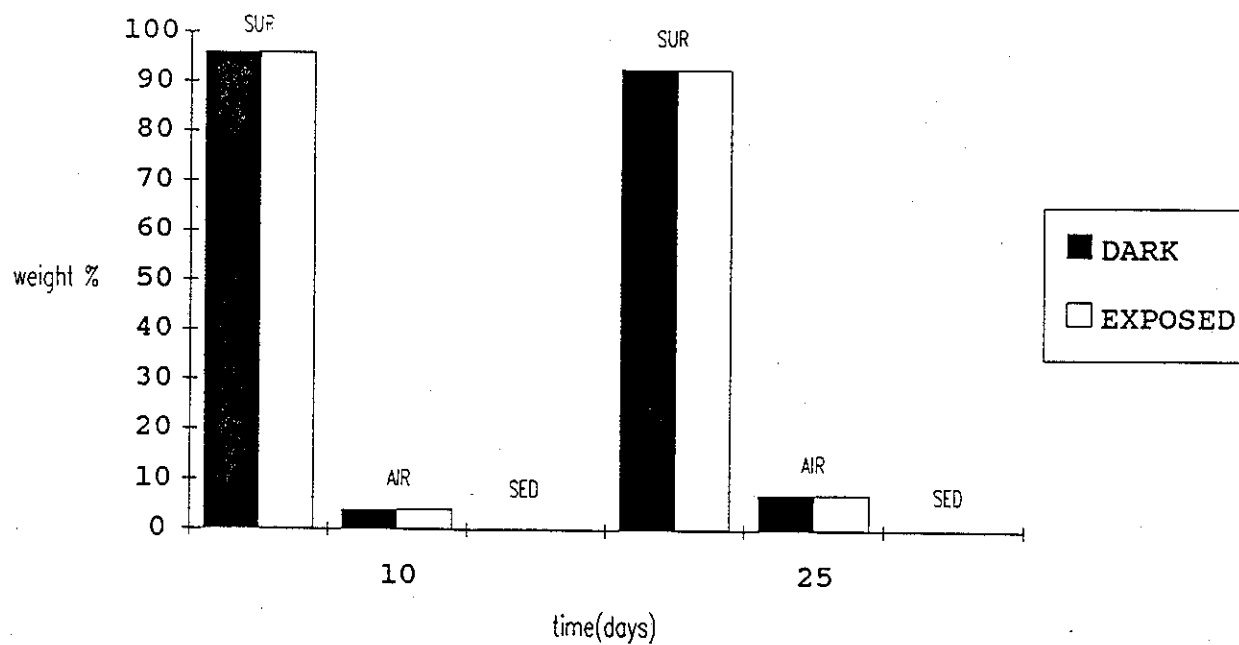


Figure 34: Mass Balance for ASMB Crude Oil.



AIR = Air
SED = Sediment
SUR = Surface

Figure 35: Mass Balance for Prudhoe Bay Crude Oil.

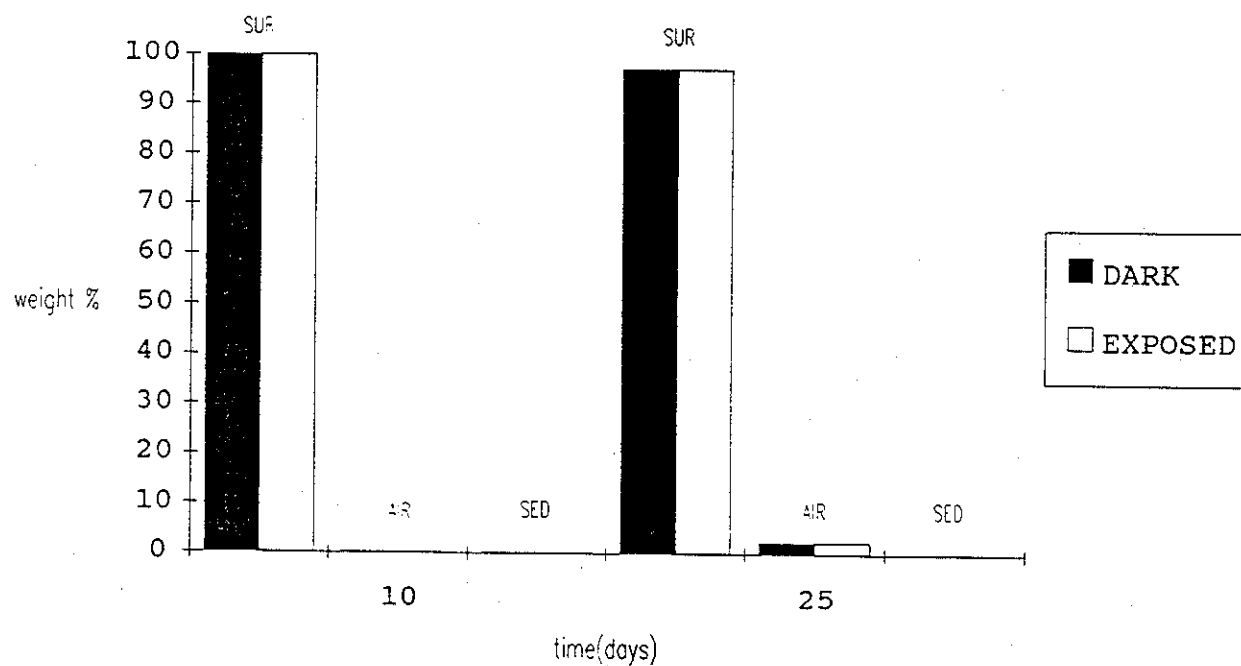


Table 9 provides data for the experiments conducted indoors under UV lamps. Trends seen in these results are similar to those obtained from experiments conducted in natural sunlight. UV irradiation of oil lead to: higher concentrations of hexane-insoluble asphaltenes; higher concentrations of oil components in the aqueous phase; and significantly increased amounts of sedimented oil.

Table 9:

Experiments Conducted Under UV Lamps

Oil	Condition	Time Hrs	Density g/mL	Viscosity cP	Oil in Water Content ppm	Asphaltene Content % Wt	Sedimented Oil %Wt
Diesel	exposed	336	0.8811	16.8	91		4.4
	dark	336	0.8521	8.4	1.9		0.04
Bent Horn	exposed	432	0.9168	224000	17.4	3.1	0.12
	dark	432	0.886	88000	0.5	1.0	0.04
California API 15	exposed	336	1.02		10.9	22.3	3.5
	dark	336	1.0111		4.9	22.1	0.02
California API 11	exposed	336	1.0206		14.7	18.9	3.5
	dark	336	1.011		14	18.4	0.003
Cold Lake Bitumen	exposed	432	1.0089		10	15.1	0.18
	dark	432	1.0082		0.4	14.6	0.06
ASMB	exposed	432	0.9402	640000	5.5	5.8	0.10
	dark	432	0.9253	368000	0.6	4.4	0.03
Bunker C	exposed	336	0.989	760000	1.2	8.3	0.08
	dark	336	0.989	691200	0.9	7.4	0.06
Prudhoe Bay	exposed	432	0.962	20000	2.7	8.7	0.10
	dark	432	0.955	11500	0.2	7.4	0.08
Hibernia	exposed	432	0.9497	288000	13.3	5.9	0.04
	dark	432	0.944	120000	0.4	3.6	0.02

Analyses of selected water samples for aldehydes and ketones are presented in Table 10. Relative to the water blank, high concentrations of aldehydes were found in the water beneath irradiated oils. The most abundant aldehydes found in the water were formaldehyde and acetaldehyde. These compounds were detected in the ppm range. Higher molecular weight aldehydes and ketones have low concentrations compared to these compounds. The relative abundance of individual compounds is clearly dependent upon the oil type and upon the irradiation source. Results from the analysis show that diesel irradiated by sunlight had a formaldehyde-to-acetaldehyde ratio of 10 while diesel irradiated under UV lamps had a formaldehyde-to-acetaldehyde ratio of only 1.5.

Table 10:

Concentration of Aldehydes and Ketones in Water Beneath Oil Layers
(micrograms/ mL)

Compound	Water Blank	California API 11 exposed outdoors 21 days	Adgo exposed outdoors 21 days	Bent Horn exposed outdoors 21 days	Diesel exposed outdoors 21 days	Diesel dark outdoors 21 days	Diesel exposed indoors 336 hours
Formaldehyde	0.47	4.27	9.37	16.54	25.7	1.3	6.94
Acetaldehyde	0.19	0.57	5.8	8.94	2.54	3.56	4.65
Acrolein	ND	ND	ND	ND	0.08	ND	0.82
Acetone	0.28	0.32	1.2	1.25	0.13	0.76	0.86
Propionaldehyde	ND	0.15	1	2.01	0.4	0.13	ND
Crotonaldehyde	ND	ND	ND	ND	ND	ND	0.53
Methyl ethyl ketone	ND	ND	0.53	0.8	0.42	0.16	ND
Benaldehyde	ND	0.14	0.19	0.08	ND	ND	0.17
2-Pentanone	ND	ND	ND	0.16	ND	ND	ND

Results from the GC-MS analyses of selected water samples are shown in Tables 11 to 18. The data indicates that a variety of photooxidation products were formed and entered the aqueous phase. Only oxygenated compounds are listed in the tables. These compounds were not found in water samples from the corresponding dark control. No attempt was made to quantify non-oxygenated compounds. Among the photooxidation products identified were aliphatic and aromatic acids, alcohols and phenols.

Table 11: GC/MS ANALYSIS	
sample: water sample from beneath diesel exposed outdoors 3 days	
compound	aqueous concentration ppm
benzoic acid	0.407
benaldehyde	0.132
phthalic anhydride	1.040
1H-inden-1-one, 2,3-dihydro-	0.810
1H-indene-1,2,3-trione	0.804
3-buten-2-ol, 4-phenyl	0.489
1-naphthaleneacetic, methyl ester	0.451
1(3H)-isobenzofuranone	0.466
1(2H)-naphthalenone, 3,4-dihydro-	0.788
pyrido[2,3-d]pyrimidin-4(1H)-one	1.866
1,3-isobenzofurandione, 4-methyl-	1.929
1,2-benzenedicarboxylic acid, 4-methyl-	3.483
phenol,2-ethyl-	1.485
2(H)-1-benzopyran-2-one, 7-methyl-	0.747
1(H)-indene-4-methanol, 2,3-dihydro-1,1di	0.917
1-indanone, 5,6-dimethyl-	4.772
1,3-isobenzofurandione, 5,6-dimethyl	2.818
1-naphthalenol, 4-methyl	4.955
9(10H)-anthracenone	1.305
	28.084

Table 12: GC/MS ANALYSIS		
sample: water sample from beneath diesel exposed outdoors 6 days		
compound	aqueous concentration	
	ppm	
phthalic anhydride	1.058	
1,3-isobenzofurandione, 4-methyl-	0.365	
1,2-benzenedicarboxylic acid, 4-methyl-	0.676	
1,3-isobenzofurandione, 5,6-dimethyl-	0.433	
1-naphthalenol, 4-methyl	4.955	
dibenzothiophene, 3-methyl-	0.330	
1,8-naphthalic anhydride	0.236	
phenol, 4,4'-thiobis[2-(1,1-dimethylethyl)-	1.148	
	9.200	

Table 13: GC/MS ANALYSIS		
sample: water sample from beneath diesel exposed outdoors 21 days		
compound	aqueous concentration	
	ppm	
benzoic acid	1.271	
1,2-benzenedicarboxylic acid	27.519	
2,3-naphthalenedicarboxylic acid	6.781	
benzaldehyde	11.204	
phthalic anhydride	29.605	
ethanone, 1-(3,4)-dimethylphenyl-	8.445	
pyrido(2,3-d)pyrimidin-4(1H)-one	2.273	
1,3-isobenzofurandione, 4-methyl-	11.059	
1,2-naphthalenedione, 6-hydroxy-	0.631	
ethanone, 1,1-(1,4-phenylene)bis-	0.776	
1,4-indol-5-ol	0.775	
1(3H)-isobenzofuranone, 5-methyl-	1.365	
1-indanone, 5,6-dimethyl-	0.901	
1,3-isobenzofurandione, 5,6-dimethyl-	17.389	
	119.994	

Table 14: GC/MS ANALYSIS		
sample: water sample from beneath diesel exposed under UV lamps for 336 hours		
compound	aqueous concentration	
	ppm	
phthalic anhydride	0.322	
1H-indole, 7-methoxy-	0.431	
1,2-naphthalenedione, 6-hydroxy-	0.498	
1,2-benzenedicarboxylic acid	1.137	
1,3-isobenzofurandione, 5,6-dimethyl-	0.830	
1H-inden-1-one, 2,3-dihydro-4,7-dimethyl-	1.071	
1H-isoindole-1,3(2H)-dione, 2-methyl-	2.415	
1,2-naphthalenediol, 1-ethyl-1,2,3,4-tetrahydro-	0.556	
benzoic acid, 4-ethyl-, methyl ester	0.711	
9H-fluoren-9-one	0.869	
1H-indene-4-carboxylic acid, 2,3-dihydro-	0.557	
1,8-naphthalic anhydride	0.696	
phenol, 4,4-thiobis(2-(1,1-dimethylethyl)-5-methyl	3.047	
	13.140	

Table 15: GC/MS ANALYSIS		
sample: water sample from beneath Bent Horn exposed outdoors 21 days		
compound	aqueous concentration	
	ppm	
phthalic anhydride	0.197	
1,2-naphthalenedione, 6-hydroxy-	0.583	
1,2-benzenedicarboxylic acid	0.870	
1H-isoindole-1,3(2H)-dione, 2-methyl-	0.833	
1,2-naphthalenediol, 1-ethyl-1,2,3,4-tetrahydro-	0.589	
	3.071	

Table 16: GC/MS ANALYSIS	
sample: water sample beneath California 11 exposed outdoors 21 days	
compound	aqueous concentration ppm
hexanoic acid, 1-methyl	2.485
benzaldehyde	2.847
hexanoic acid	2.290
heptanoic acid	2.606
1,2-benzenedicarboxylic acid	32.502
2,5-cyclohexadiene-1,4-dione, 2-octadecyl-	12.920
cyclohexaneethanol, 4-dimethyl-,	1.688
heptadecanoic acid, 16-methyl-, methyl ester	0.284
	57.622

Table 17: GC/MS ANALYSIS		
sample: water sample from beneath California 15 exposed outdoors 21 days		
compound	aqueous concentration	
	ppm	
phthalic anhydride	2.988	
1,2-naphthalenedione, 6-hydroxy-	0.583	
1,2-naphthalenediol, 1-ethyl-1,2,3,4-tetrahydro-	0.589	
	4.159	

Table 18: GC/MS ANALYSIS		
sample: water sample beneath California 15 exposed under uv lamp 336 hours		
compound	aqueous concentration	
	ppm	
heptanoic acid, ethyl ester	1.112	
octanoic acid, 2,4,6-trimethyl-, methyl ester	0.351	
nonanoic acid, ethyl ester	0.668	
nonanoic acid, 2,6-dimethyl-, methyl ester	3.032	
undecanoic acid, ethyl ester	0.507	
benzoic acid	0.397	
phenol, 4,4'-methylenebis-	0.236	
1(3H)-isobenzofuranone, 3-ethoxy-	1.913	
1,2-naphthalenedione, 6-hydroxy-	0.583	
1,2-naphthalenediol, 1-ethyl-1,2,3,4-tetrahydro-	0.589	
	9.387	

No strong quantitative correlation was found between any simple measure of overall oil composition (aromatic, alkane, resin, and asphaltene content) and the photo-reactivity of oil. Figures 36 to 37 show the carbon content of water beneath oils irradiated for 21 days and aromatic and sulfur contents of oil, respectively. Although the data is limited, it would suggest that oil with low sulfur contents are more susceptible to photooxidation. Data from previous research indicates that sulfur compounds inhibit photooxidation (Larson et al., 1977).

Figure 36: Carbon Content of Water Phase versus Aromatic Content of Oil.
Oils exposed 21 days.

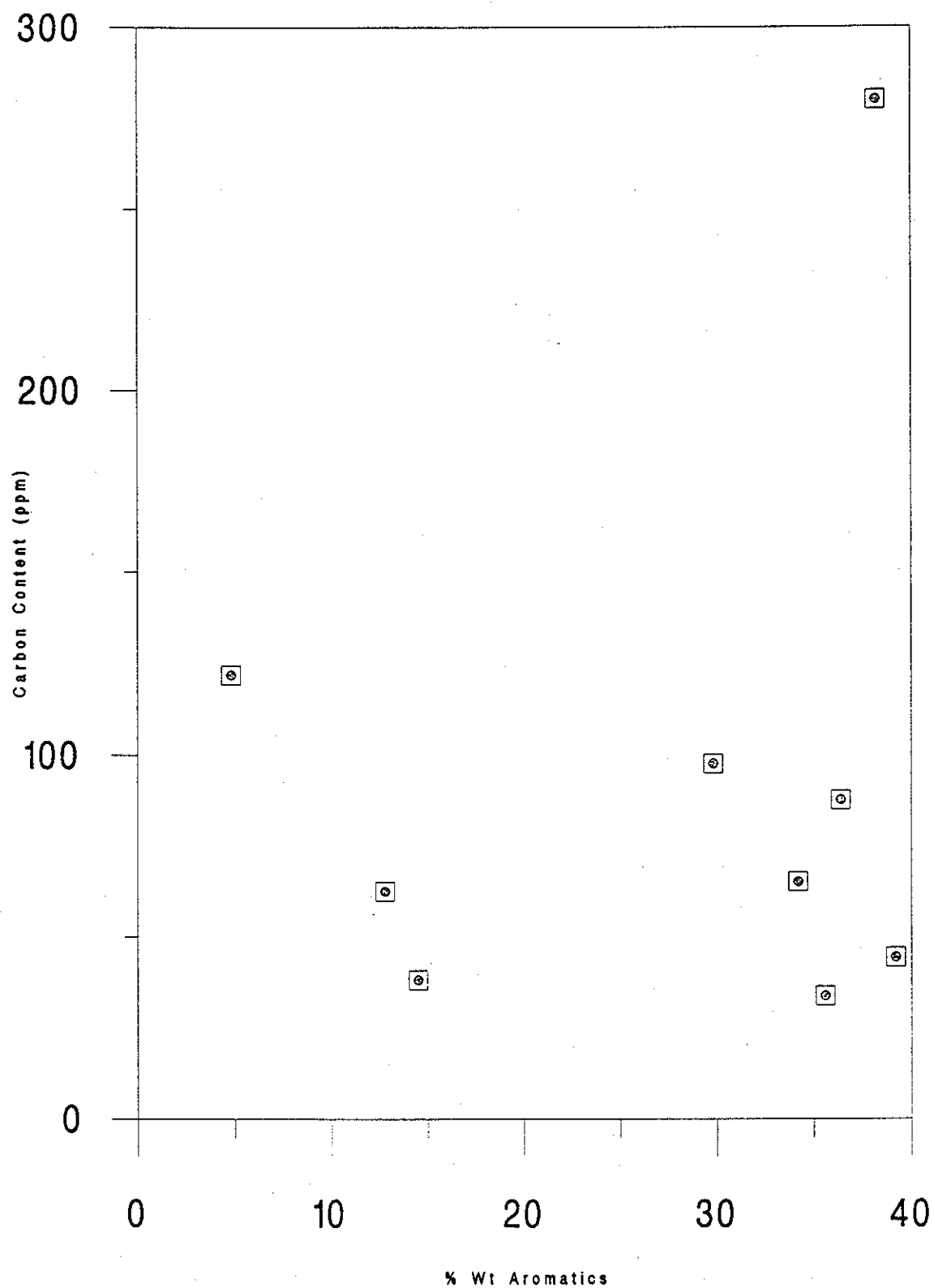
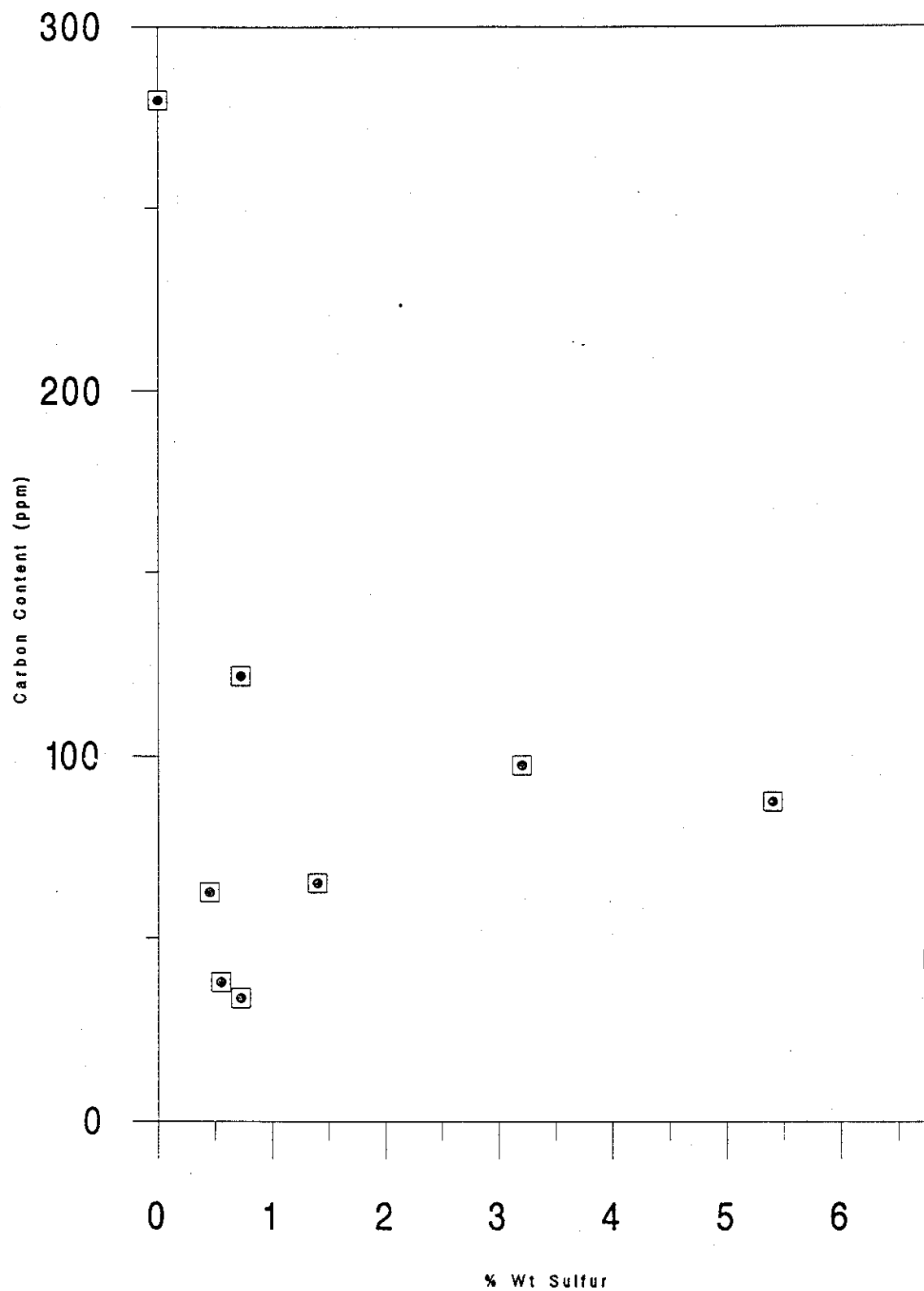
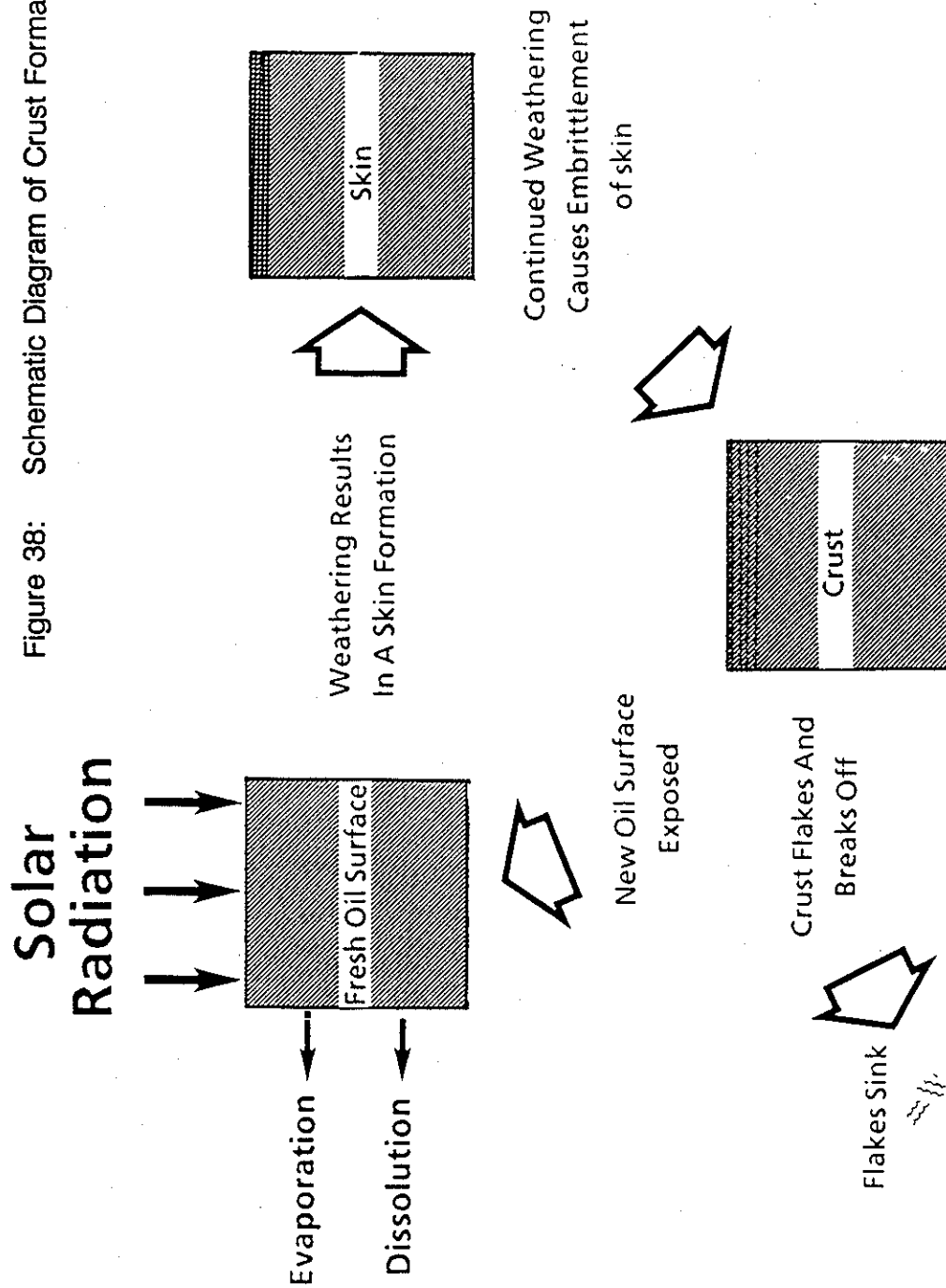


Figure 37: Carbon Content of Water Phase versus Sulfur Content of Oil.
Oils exposed 21 days.



From the physical changes observed in oils (Table 4) and from the results obtained, it is concluded that photo-induced reactions are responsible for the formation of materials which encrust oil. Figure 38 is a simple schematic diagram that illustrates how oil "crust" is formed. As oil weathers, a "skin" of dense material forms at the air-oil interface. This skin was observed to form on oils that were photolysed as well as on oils that were shielded. If this material is subjected to photolysis, it becomes embrittled thus forming a hardened crustal material. No crust was formed on oils kept in the dark. Further exposure causes the crustal material to form flakes which eventually break off and sink, thus exposing a new oil surface. The crusts observed in this study are similar in description to those found on tar balls by Morris et al. (1977).

Figure 38: Schematic Diagram of Crust Formation.



CONCLUSIONS

The importance of photolysis as a weathering process will depend very much upon the type and composition of the oil. This study has identified several oils which are extremely sensitive to photooxidation, and it has demonstrated how photo-induced reactions can influence the fate and behaviour of these oils. Photolysis induced changes in physical properties and resulted in the formation of products that increased the amount of oil entering the water column. Among the photooxidation products identified in water were aliphatic and aromatic acids, alcohols and phenols.

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